VOLUME 34 MARCH 1956 NUMBER 2

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Printed in Canada *by* University of Toronto Press

Canadian Journal of Technology

Issued by THE NATIONAL RESEARCH COUNCIL OF CANADA

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STUDIES IN ELECTROSTATICS[1]

A. PREVENTION OF ELECTROSTATIC CHARGES ON POWDERS
B. PREVENTION OF EXPLOSIONS DURING HAND OPERATIONS ON DETONATORS

BY P. E. BRAID,[2] R. C. LANGILLE,[3] AND ANNA M. ARMSTRONG[4]

ABSTRACT

Electrostatic charges which frequently occur when powders are stirred, sieved, etc., may be prevented by using rough-surfaced rather than smooth-surfaced vessels or alternatively by coating the vessels, spoons, sieves, etc., with the powdered material itself by means of a suitable adhesive. Occurrence of explosions during hand operations on detonators was attributed to a spark discharge from the operator's body. Conditions favoring sparking were dry clothing for charge generation combined with moist hands to cause contamination of the supposedly insulated manipulating tool. Modification of the tool and/or positive grounding of the operator's body were recommended as preventive measures.

STUDIES IN ELECTROSTATICS

The problem of the accidental generation of electrostatic charges is often a troublesome one, and in some cases, as in the handling of explosives, it can be distinctly hazardous. In the course of research on explosives it was necessary to investigate this problem on more than one occasion and the results given here are from investigations on two separate aspects of the problem, namely, elimination of the small but troublesome charges which make manipulation of small quantities of certain dry, powdered materials very difficult, and elimination of spark formation during operations on detonators.

A. PREVENTION OF ELECTROSTATIC CHARGES ON POWDERS

INTRODUCTION

In routine investigations of properties of explosive materials, explosives of various types were subjected to a standard preparative treatment which involved grinding and sieving of the material through a 100-mesh sieve, drying at 50° C., and resieving to remove aggregates formed in the drying operation. Many substances may be thus dried and subsequently sieved with

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little or no evidence of generation of electrostatic charges (6). However, many other substances, notable examples among explosives being tetryl and RDX, produce a very high degree of electrification under this treatment. Dried, powdered tetryl will frequently clog a 100-mesh sieve so quickly that little material passes through. Such substances will also adhere tenaciously to measuring spoons and various other surfaces, whether metallic or non-metallic. This renders manipulations such as weighing, sieving, measuring, and transfer of small quantities very difficult. Several methods of discharging the material may be employed such as: use of radioactivity (4, 7); use of neutralizing charges (8); exposure to very moist air (5, 8); or leaving it alone for a sufficiently long time. However, the complete removal of residual charges is often very difficult (5). Furthermore, none of these curative methods are very satisfactory, since stirring, spooning, or sieving generally brings back the charge almost instantly. Methods of preventing formation of the charge (the use of a high-humidity atmosphere being, of course, unfeasible in the present instance) were therefore investigated.

Experimental

Tests showed that, when rubbed on powders, rough surfaces produced much smaller charges than smooth surfaces of the same material. Thus, tetryl rubbed on smooth and very rough tinfoil, on polished and slightly roughened copper foil, and on glazed and unglazed paper, showed the effect. It had previously been found that when powdered RDX contained in a glazed porcelain crucible was removed by a small metal scoop and poured onto a surface, troublesome electrostatic charges were generated. When the porcelain crucible was replaced by the bottom of a Soxhlet extractor thimble and the scoop was made of the same material (the bowl of the scoop being formed by hammering a flat spoon-shaped piece of thimble into a depression in a lead block) generation of charges on RDX was greatly reduced.

The explanation of the effect is probably that smooth surfaces make frictional contact with the particles of powder, whereas rough surfaces drag powder over powder; therefore friction is mainly between particles of the same substance, and electrification is minimized.

Since it is not always possible to provide rough surfaces (e.g., when sieving of a powder is required), and since the above method is equivalent to coating surfaces with the material to be handled, this expedient was tried. Smooth objects such as watch glasses and metal spatulas were painted with rubber tire cement diluted with an equal volume of benzene, and allowed to dry for 20 min. Finely powdered tetryl was then brushed on. A sieve was coated by painting it with a 50–50 mixture of rubber cement and xylene (benzene being too volatile for this), blowing off the excess with compressed air, and allowing to dry overnight. Powdered tetryl was then brushed on.

A series of tests was made to determine the effectiveness of the coating procedure.

1. A few grams of tetryl were left in a large tetryl-coated watch glass until

it had no charge (see Test 5 below). With a single stroking by an insulated strip of clean copper sheet, both sheet and tetryl became charged. A gold-leaf electroscope indicated several hundred volts on the copper sheet.

2. With many strokings of the tetryl by a similar copper sheet tetryl-coated, no electrification occurred.

3. Neutral tetryl caused to slide gently on a grounded copper tray, or a watch glass or sheet of paper, became charged at once.

4. Neutral tetryl caused to slide on tetryl-coated copper, glass, or paper showed no charge whatever.

5. When tetryl was poured from a tetryl-coated watch glass on to a small copper tray attached to the top of the electroscope, a charge was produced on the electroscope—no doubt by the friction of the tetryl falling on the copper. When this tray was tetryl-coated no charge was produced by the above procedure, but when tetryl stroked with copper as in Test I was poured on the tray, a charge was produced at once. This tetryl-coated tray was therefore always used in the tests.

6. One-half of an 8-in. diameter, 24-mesh copper sieve was tetryl-coated, and the other half left bare. Neutral tetryl (i.e., left on the sieve for several hours) was sifted onto the coated tray attached to the electroscope. It caused no (or sometimes very slight) electrification. The same procedure with the uncoated part of the sieve produced a high degree of electrification.

7. It was impossible to pour neutral tetryl from an uncoated glass or copper dish (whether grounded or not) without the tetryl becoming charged by merely passing over the edge of the vessel.

All the above tests were carried out with aluminum oxide, with results identical to those given above. It seems very probable that many other powders of high surface resistance would behave in the same way. While charges can be produced by asymmetric rubbing of surfaces of the same material (3), measurable charges are unlikely to be produced in this way under the conditions given here. Although both of the methods for minimizing charges described here result in a great reduction in charge generation, the method of coating the surfaces is the more completely effective.

Such coatings were found to be reasonably durable and could be heated in the oven (50° C.) a number of times without losing their effectiveness. With this heat treatment the occurrence of adsorbed films which might alter the nature of the coated surfaces was avoided. However, it is possible that with materials which are subject to gradual oxidation or other alteration on continued exposure to air (2, 11) the coated surfaces might require frequent replacement.

B. PREVENTION OF EXPLOSIONS DURING HAND OPERATIONS ON DETONATORS

Introduction

During the manufacture of detonators it was found that occasional explosions occurred at the time that a seated operator approached them with

the hand to perform an operation. The results of a series of experiments established that the explosions were caused by the grounding of an electrostatic charge through the detonator, and that the charge must be generated by the operator herself within a short time of entering the room, since the room was maintained at about 70% relative humidity. Furthermore the operator must be a person with rather moist hands, since only under these circumstances could she contaminate the supposedly insulated stick which was employed in the operation sufficiently to provide a conducting path for discharge to ground. It was corroborated that the explosions were found to occur soon after a group of workers came on shift and that they tended to recur with certain individuals. The explanation appeared to be that when a new group of workers came on shift they would be wearing clean dry clothing which they had just previously put on. Electrostatic charges would be generated on the workers' bodies by their frictional contact with the varnished wood seats. Those workers with very moist hands would contaminate their wood-and-beeswax tool, which is used to place a disk of paper on the detonator, and thus provide a preferred leakage path for the charge via the detonator to ground.

The detonators were of 5.0 grain size, for use in fuses (No. 119, Mk. $1\frac{1}{2}$) of high-explosive shells. They consisted of a copper cup (approximately $\frac{1}{4}$ in. in diameter and $\frac{1}{4}$ in. deep) which was filled mechanically with a mixture of lead azide, lead styphnate, and aluminum powder. The surface of the filling was then shellacked, covered with a small paper disk, then with a metal annulus, and then crimped mechanically.

For the operation of placing the paper disks in position the workers, dressed in cotton clothing, sat at enamelled-top tables, on metal stools fitted with varnished wood seats. The floors were of mastic. The detonators, on a pad of black felt in a papier mâché tray, were slid along the table until they rested on a pad of conducting rubber which in turn stood on a grounded copper plate. The operator was provided with a "kittstick"—a piece of wood 5/16 in. in diameter and 9 in. long with a slug of beeswax about 1 in. long attached to the end. With the sticky beeswax tip she picked up a paper disk and placed it on the detonator, re-forming the wax tip from time to time by working it between her finger and thumb. The series of experiments which led to an explanation of the circumstances for spark formation are given below.

Several of the factors which led to the situation described here have been understood and discussed on previous occasions. Thus it has been stated that cotton and other approved fabrics should be exposed to the humid atmosphere of the workroom for at least 10 min. to attain equilibrium or they may give rise to dangerous electrostatic charges (1). Furthermore frictional contact with ungrounded seats may generate charges of well over 15,000 volts on the body (1). Trouble with occasional explosions was also experienced in detonator factories in England (10). There the solution of the problem involved making routine conductivity measurements on the personnel. In the present instance, however, a simpler alternative was desired.

Experimental

(1) One subject, after two or three one-eighth circle turns of the body back and forth on a wooden stool, brought a metal screwdriver close to a small heap of lead styphnate on a grounded copper plate. The charge detonated at once. The spark was 2 or 3 mm. long. This was repeated a number of times but detonation did not always occur and some subjects could never get a detonation.

(2) To obtain more consistent and reproducible charges a small Wimshurst machine was used with the spark gap between 2.5 cm. balls adjusted to 4–5 mm. (a distance less than the length of spark often obtained, on certain days, from the fingers of some people as a result of their ordinary movements about a room). The machine was used both with and without the two condensers of approximately 0.001 μf. capacitance with which such machines are provided to enhance spark production.

Without the condensers, styphnate lightly stemmed in holes 1.5 mm. diameter and 3 mm. deep in a brass plate could be nearly always detonated, especially when the brass plate was covered with a piece of vinylited thin cardboard with a pinhole over each hole.

(3) Even with the condensers attached no detonation could be obtained through the wooden stick without the wax (nor, of course, with the wax) when these were left in ordinary air.

(4) After the kittstick had been left for half an hour in air of humidity 80%, detonation could be obtained with the condensers through the wooden stick but not through the wax.

(5) A subject with naturally moist hands was asked to handle the wooden stick thoroughly. Detonation was obtained through the stick. After he had kneaded the wax with finger and thumb, and thoroughly handled the stick, detonation was obtained through both stick and attached wax. The kittstick had been left in ordinary air, but the condensers were attached to the Wimshurst and the spark gap increased to about 5 mm.

(6) A tray (top of a turned wooden box, with grain vertical) containing a felt pad about 3/16 in. thick was used to support the metal plate containing the styphnate. When this tray and pad had been left in air at something less than 80% moisture for about 30 minutes sparks could be easily passed through metal, felt, and tray to a grounded plate, but only when the spark gap was increased to about 6 mm. and the condensers were attached.

(7) Next a combination of the whole chain of conductors was tried. The wooden tray with felt and the kittstick with wax were left half an hour in a humidity of 80%; the wood of the kittstick was quickly handled and the wax kneaded by the subject of Experiment 5, the tray with felt was quickly brought into laboratory air and grounded, and the plate with styphnate placed on the felt. Detonation was obtained through the whole set when the spark gap was increased to about 7 mm. and the condensers were attached to the machine.

(8) Experiments were then made to reduce the capacity and the spark gap. Finally, with the human body as the only capacity, and with the machine

adjusted so that the spark from a 2 cm. ball held in the hand to a grounded 3 cm. ball was 5 mm. long, several detonations were obtained through the whole series—hand, kittstick with wax, and tray with felt—provided the last two were treated as in Experiment 7.

The detonation occurred as the point of the wax slug approached the pinhole over the styphnate, apparently exactly as the explosion had occurred in the factory. In these experiments a subject, wearing army boots, sitting on a wooden stool with his feet on the rungs, took a spark from the Wimshurst machine on to his left hand, removed his left hand well away from the machine and only then approached the kittstick, held in his right hand, to the styphnate. The charge on the body in this case was about 17,000 volts, again less than that frequently obtained by some people by ordinary movements in a room. It has been pointed out that the discharge of a spark through a resistance such as the human body has a greater incendive effect than the same spark discharged without the resistance (9).

(9) In a cupboard in which the humidity was 80% an electric charge leaked off a homemade electroscope quickly. It behaved similarly in the humidified room in which the detonators were handled. However, it was possible to recharge it as easily as in ordinary air by rubbing sealing wax on the clothes or hair *during the first few minutes in the cupboard*; later the clothes and hair became too damp to produce electrification easily.

(10) A round glass flask about 7 cm. in diameter, covered with tinfoil, with a capacity of about 4×10^{-6} microfarads (8) was charged to about 20,000 volts. In many trials no detonation of styphnate could be produced by a direct spark from it. (The capacity of the human body is about 3×10^{-4} μf. (8, 9). The capacity of kittstick or tray with felt must be considerably less than that of the flask.)

Conclusions (Part B Only)

Experiments 2 to 8 show that a combination of circumstances such as may occasionally arise in a room of high humidity with an operator who has abnormally moist hands will provide a sufficiently conducting circuit for electricity, with a voltage of 17,000 volts and with a capacity equal to that of the human body, to detonate styphnate.

Experiment 1 shows that sufficient voltage can be provided by a few turns of the body on a wooden stool to detonate styphnate through a metal conductor, and it is common knowledge that ordinary movements of the body about a dry room may occasionally produce charges of 20,000 volts and more.

With regard to Experiment 4 Silsbee points out that the surface resistance of an insulator such as wood may decrease by a factor of 10^6 in going from an atmosphere of 30% relative humidity to one of 80%. Such materials acquire a surface layer of moisture which always contains enough dissolved material to provide a fair degree of electrical conductance. However, a few materials including waxes fail to acquire such films in humid atmospheres (8).

Body sweat contains water, sodium chloride, cholesterol, fats, fatty acids,

traces of albumin and urea, and other minor constituents. Therefore in Experiment 5 the handling of a material such as wood by a person with naturally moist hands would soon result in the material becoming coated with a film of moisture which contained a relatively large amount of conducting substances. Similarly, the organic constituents of sweat would penetrate the surface layers of the wax slug, altering the nature of the surface sufficiently that the existence of an adherent conducting moisture film became possible.

Experiment 9 shows that although it may be difficult to produce static charges on the body when the clothes have become damp from humid air, a humidity of 80% in the air is no deterrent to a brief electrification provided the clothes are dry, as would be the case when the operators first come on the shift.

Experiment 10 shows that it is extremely unlikely that sufficient charges could originate from friction either on the wood or on the wax of the kittstick or from the sliding of the trays on the enamelled tables, for the capacities of these objects must be much too small.

Two methods of preventing the occurrence of accidental detonations were suggested. The operators could be grounded by a metal bracelet attached at the wrist. Alternatively the operator's "kittstick" could be provided with deep corrugations running round the stick, the valleys being impregnated with paraffin. The upper part of the stick would still become contaminated from being held and the lower part from re-forming of the beeswax with the left hand. However, when brought near the detonator the stick is held only at the upper end above the grooves and the former continuous leakage path induced by perspiration would be interrupted. The sticks should also be replaced or at least checked by a comparative resistance measurement from time to time. Both grounding of the operator and modification of the "kittstick" might well be employed.

In the factory in which the incidents which initiated this investigation occurred, the first suggestion was considered to have psychological disadvantages and was not put into practice; the "kittsticks" were, however, modified in accordance with the second suggestion and no further mishaps occurred.

SUMMARY

A. (i) If a powdered material tends to become electrostatically charged when handled, the effect can be greatly reduced by providing containers and implements with rough surfaces. In this way the manipulations result in powder being dragged across powder, friction between powder and other material being minimized.

(ii) If a powdered material tends to become electrostatically charged when handled, the effect can be very greatly reduced by coating containers and implements with a layer of the material being handled. Containers were coated by painting them with dilute rubber cement, allowing it to become nearly dry, and then brushing the powder onto this surface.

B. Persons sitting on wooden stools could, by making frictional contact with the stool by normal body motions, generate sufficient electrostatic charge to detonate sensitive explosives if they approached the explosive in such a way that the charge was grounded through it. A charge of this magnitude could be generated even in a room of high humidity within a short time after the operator entered the room. Suggested means of avoiding such explosions were to make the operator's normally non-conductive manipulating tool resistant to short-circuiting by perspiration and/or to provide positive grounding for the operator's body.

ACKNOWLEDGMENTS

The authors are indebted to the late Dr. F. B. Kenrick, former Head of the Department of Chemistry, for his guidance throughout these investigations. They also wish to express their sincere appreciation to Dr. G. F Wright, also of the University of Toronto Department of Chemistry, for his interest. This work was supported by a National Research Council wartime grant.

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A SEMIMICRO GELOMETER[1]

By D. A. I. Goring[2]

ABSTRACT

An instrument has been developed for the simultaneous measurement of the breaking strength and rigidity of a gel 4 ml. in volume. Its performance has been studied under a variety of conditions of operation for gelatin, carrageenin, and agar gels. Reproducibility was ±6% for gel strength and ±4% for rigidity.

INTRODUCTION

Several devices have been described for determining characteristic properties of gels. Some measure the force required to break the gel (1, 2, 7, 13); others measure the gel's resistance to deformation without rupture (3, 4, 5, 8, 9, 10, 11, 12, 13, 14). The present communication describes an instrument which permits simultaneous measurement of the strength and rigidity of a gel. Its performance with gelatin, carrageenin, and agar gels is reported.

The instrument was developed from an earlier model previously described briefly (6). It is similar in principle to the Tarr–Baker tester (1) and the Bloom gelometer (10). Breaking strength is estimated as the force required to rupture the surface of the gel with a cylindrical plunger. Rigidity is calculated from the depression of the gel under known load. Measurements can be made rapidly with 4 ml. of gel.

EXPERIMENTAL

The Gelometer

The gelometer is shown in Fig. 1. A motor-driven plunger depresses the gel, which rests on the pan of a 500 gm. dietary balance. As the pointer of the balance moves it pushes a light indicator needle mounted on a pivot in the center of the scale. At the point of rupture, the plunger penetrates the gel and the pointer moves momentarily backwards leaving the needle at the maximum point. The motor is stopped and the scale reading indicated by the needle is then the breaking strength, G, of the gel.

Four interchangeable Bodine motors (Type KC1—Capacitor Reducer) were used. The pitch of the screw was 0.907 mm./turn allowing plunger speeds of 0.36, 0.88, 1.45, and 2.21 mm./sec. The speeds of the motors were suitably constant.

A metal strip supported a shoulder on the screw shaft of the motor and eliminated any vertical play in the plunger. The plunger was mounted on a piece of $\frac{3}{8}$ in. square brass rod which was held from turning by a loose-fitting aluminum guide. Plungers were approximately 15 mm. long and 4, 6, or 8 mm.

[1]*Manuscript received November 4, 1955.*
Contribution from the Maritime Regional Laboratory, National Research Council, Halifax, N.S. Issued as N.R.C. No. 3880.
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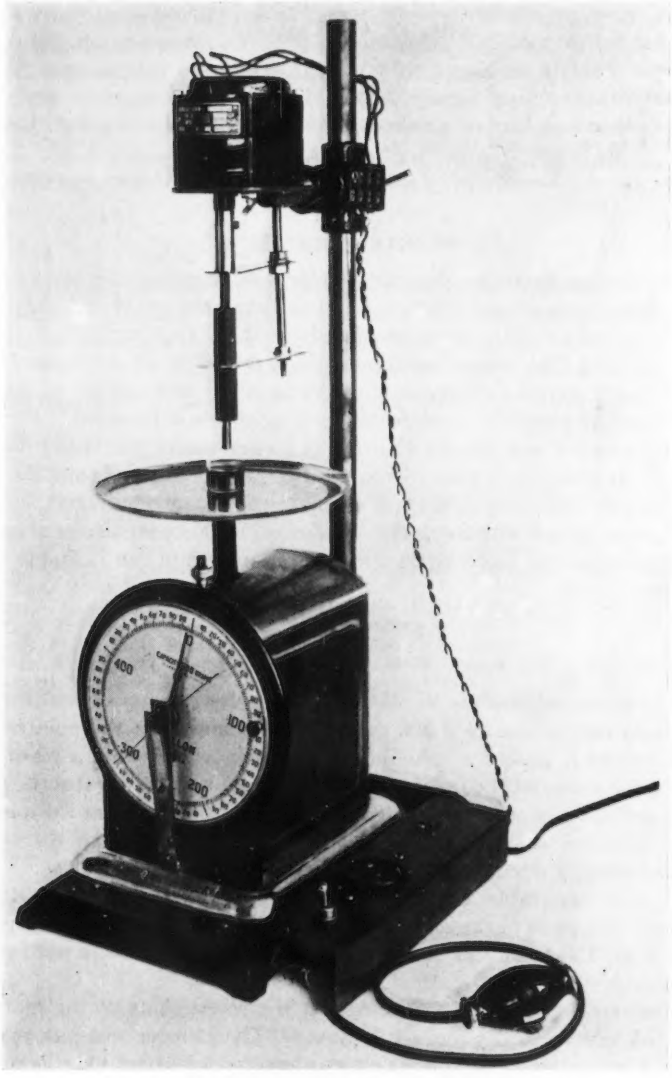

FIG. 1. Photograph of gelometer (by F. G. Mason).

in diameter; they were slightly conical in shape to give a clean break once the gel had been punctured.

Gels were made in the cylindrical, 5 mm. beakers used in the Beckman pH meter. Beakers were selected with a uniform diameter of 20.5 ± 0.13 mm. With the beaker on the balance pan, the scale was adjusted to zero before the measurement was made.

The indicator needle was made of No. 7 piano wire and was mounted as shown in Fig. 2. By adjusting the tension of the phosphor-bronze strip, the

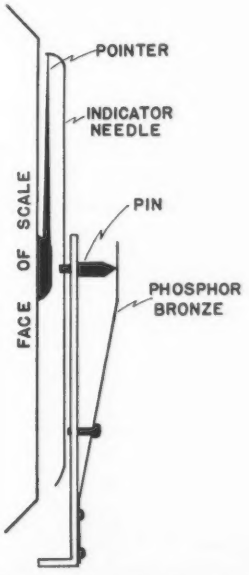

FIG. 2. Mounting of indicator needle.

force required to move the needle was set so that when a weight was placed on the pan, no detectable difference was noted in the position of the pointer with or without it pushing the needle.

To determine the rigidity, the movement of the pointer was timed with a stop watch between a reading of 10 gm. and X, approximately one half of the estimated gel strength. The distance of descent, d, of the plunger during the timed interval was computed from the speed of the plunger. The movement of the pan, p, between the readings 10 and X was obtained by multiplying $X - 10$ by a calibration factor relating the movements of the pan and pointer. (This factor was determined by timing the movement of the pointer when the pan, with no gel, was depressed directly by the plunger.) The depression, g, of the gel was given by

$$g = d - p, \qquad [1]$$

and an empirical coefficient of rigidity, R, was obtained from

$$R = (X - 10)/g. \quad [2]$$

The units of R were gm./cm.

Preparation of Gels

As pointed out by Hamer (7), the precision of a gelometer usually exceeds the reproducibility of gels. Therefore great care was taken in making and handling the gels.

The gelatin and agar samples were Difco Bacto-Gelatin and Bacto-Agar respectively. The carrageenin was a sample of high gel strength material supplied by the Seaplant Chemical Corporation. Concentrations for carrageenin, agar, and gelatin were respectively 1.5%, 2%, and 6%. The solvent used throughout was 0.2 M KCl + 0.05 M CH_3COONa.

Samples were dissolved at 100° C. Exactly 4 ml. of the solution was transferred hot to a 5 ml. beaker with a preheated 5 ml. syringe. The beaker was covered with a glass plate and the gel allowed to cool and set for an hour. Condensation was then wiped from the plate, the beaker re-covered, and the gel aged overnight. Gels were aged and measurements made in rooms thermostated at 20° C. for carrageenin and agar and 10° C. for gelatin.

Initially the gel was inverted before measurement to expose a fresh surface (6). However, it was found that identical results were obtained if (*a*) the gel was kept covered during aging, and (*b*) the surface was cut near its circumference to a depth of 1 mm. with a cork-borer of suitable size. The depth of the cut did not affect the result. Cut and uncut gels had the same breaking strength but R was greater for uncut gels. In all measurements reported here, the aged gels were cut to a depth of 1 mm. immediately before measurement.

RESULTS

The results for G and R are given in Tables I–IV. Mean deviations are also given. Measurements were made at the four plunger speeds (Tables I and II) with the plunger 6 mm. in diameter. Variation of plunger size (Tables III and IV) was studied at the speed of 0.36 mm./sec. for carrageenin and agar; as discussed later a speed of 0.88 mm./sec. was used with gelatin.

TABLE I

VARIATION OF GEL STRENGTH WITH PLUNGER SPEED

	Plunger speed, mm./sec.							
	0.36		0.88		1.45		2.21	
Gel	G, gm.	Mean dev., %	G, gm.	Mean dev., %	G, gm.	Mean dev., %	G, gm.	Mean dev., %
Gelatin	187	9.5	182	6.5	194	9.7	247	13.0
Carrageenin	203	9.4	209	6.1	205	7.3	217	3.3
Agar	219	3.3	254	3.6	283	5.8	300	1.8

TABLE II

VARIATION OF RIGIDITY WITH PLUNGER SPEED

Gel	Plunger speed, mm./sec. 0.36 R, gm./cm.	0.36 Mean dev. in g, %	0.88 R, gm./cm.	0.88 Mean dev. in g, %	1.45 R, gm./cm.	1.45 Mean dev. in g, %	2.21 R, gm./cm.	2.21 Mean dev. in g, %
Gelatin	461	2.4	407	2.7	450	2.4	437	5.1
Carrageenin	685	4.6	680	4.4	714	6.9	658	4.7
Agar	1125	5.5	1149	5.3	1319	7.1	1200	8.6

TABLE III

VARIATION OF GEL STRENGTH WITH PLUNGER DIAMETER

Gel	Plunger diameter, mm. 3.9 G, gm.	3.9 Mean dev., %	6.0 G, gm.	6.0 Mean dev., %	8.1 G, gm.	8.1 Mean dev., %
Gelatin	98	11.1	182	6.5	253	3.8
Carrageenin	103	5.2	203	9.4	367	3.5
Agar	103	2.3	219	3.3	361	3.5

TABLE IV

VARIATION OF RIGIDITY WITH PLUNGER DIAMETER

Gel	Plunger diameter, mm. 3.9 R, gm./cm.	3.9 Mean dev. in g, %	6.0 R, gm./cm.	6.0 Mean dev. in g, %	8.1 R, gm./cm.	8.1 Mean dev. in g, %
Gelatin	224	2.4	407	2.7	800	4.3
Carrageenin	404	2.3	685	4.6	1103	3.2
Agar	610	2.9	1125	5.5	1607	4.8

About 70 individual gels were made at one time from a single solution and these were set and aged simultaneously. Ten were measured for each set of conditions. Any reading which was <0.8 or >1.2 times the mean was discarded and the remainder re-averaged. This caused 4.7% of the G values and 2.1% of the R values to be rejected.

DISCUSSION

The instrument was simple to use and the operator could easily measure 100 gels in a day. Values of the mean deviation for gel strength were small considering the nature of the measurement and the small volume of gel used. Errors in G were greatest for gelatin. When measured at 20° C., the gelatin gels did not break satisfactorily. The plunger gradually pushed further into the gel and at no time did the pointer stop or move back. A cleaner break was obtained at 10° C. This difficulty was greatest at the slowest plunger speed. Accordingly, a faster motor was used when the change in plunger diameter for gelatin (Table III) was being studied. The effect was not found in carrageenin or agar gels which broke sharply, under all conditions.

The reproducibility of the rigidity was good. Even with agar, in which values of g (Eq. [1]) were less than 1 mm., errors in R were comparatively small.

For a perfectly elastic gel, there should be no change in G and R with increase of plunger speed. This was found true for R (Table II) which was constant within experimental error for the range of speeds studied. As shown in Table I, the gel strength for gelatin and agar increased by a factor of 1.3 for the full range of speeds; the increase with carrageenin was smaller. A similar effect has been noted by Benarie (2) in measuring the tensile strength of gels. The effect is probably due to a combination of elastic and plastic behavior of the gel. Penetration is then a function not only of the force applied but also of the time that the force is allowed to act. The unsatisfactory results obtained with gelatin at 20° C. could be due to a relative increase of the plastic response at this temperature.

Empirically, G could be considered related to the radius, r, of the plunger by $G = r^x$. Logarithmic graphs of G vs. r were linear within experimental error. Values of x for gelatin, carrageenin, and agar were 1.31, 1.75, and 1.73 respectively. Thus, as might be expected, the gel strength was proportional to a function of the plunger size which was a combination of the circumference and area. A similar treatment for rigidity gave x as 1.75, 1.42, and 1.33 respectively for gelatin, carrageenin, and agar. The interpretation of these results in absolute units of elasticity and tensile strength is difficult (*a*) because of the relatively large size of the plungers compared with the volume, and (*b*) because of the probability of plastic response of the gel. However, the reproducibility is such that figures obtained under a set of standard conditions may be used as reliable empirical measurements of breaking strength and rigidity. For routine measurements of carrageenin gels, a plunger speed of 0.36 mm./sec. and a plunger diameter of 6 mm. were found most suitable.

ACKNOWLEDGMENTS

The author is indebted to Mr. L. Stoloff of the Seaplant Chemical Corporation for suggesting the basic design of the instrument, Dr. E. Gordon Young for help and advice in preparing the manuscript, and Messrs. H. F. Roberts and J. MacAulay for technical assistance.

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CALCULATED RADIATION CHARACTERISTICS OF SLOTS CUT IN METAL SHEETS. II[1]

By James R. Wait[2] and R. E. Walpole

ABSTRACT

Theoretical radiation patterns are presented for antennas consisting of a notch cut in the edge of a perfectly conducting half-plane and a vanishingly thin elliptic cylinder. The principal plane patterns for these two cases are found to be very similar. The conductance of the notch is also considered.

INTRODUCTION

The radiative characteristics of slots cut in metal surfaces are now extensively utilized in flush mounted antenna systems. For purpose of design, the surface on which the slot is cut is often assumed to be flat and infinite in extent. The radiation diffracted round the edges is thus neglected. This can be a serious source of error. When the slot is cut near the edge of a large metal sheet or plate it is a reasonable approximation to represent the surface by a perfectly conducting half-plane. If the width of the sheet is not large, a better approximation would be a metal ribbon or a vanishingly thin elliptic cylinder of infinite length.

Rather detailed calculations have been recently presented in Part I (7) for narrow slots located on half-planes and ribbons. The slots in this case were considered to be axial, that is, the slots were considered to be parallel to the edges of the half-plane and ribbon. It was shown that the azimuthal radiation patterns were independent of the lengthwise voltage distribution in the slot. Furthermore, as the axial slot approaches an edge, the calculations indicated that the azimuthal or E plane patterns became omnidirectional. In this case, the elevation or H plane patterns were determined solely by the lengthwise voltage distribution in the slot. The theoretical work mentioned above has recently been followed up by extensive experimental measurements which showed good agreement with the theory (1).

Another interesting case is when the direction of the slot is transverse to and located at the edge of the half-plane or ribbon. An antenna of this type has been termed a "notch". The radiation properties of notches cut in the edge of metal sheets have been discussed by Johnson (2) who showed that they are very versatile radiators with useful wide-band properties. Johnson's analysis was based on finding the distant field of a current element on the bisector of a corner reflector, using the method of images. Although the image technique is only valid if the corner reflector angle is a submultiple of π, he states that the

[1]*Manuscript received October 26, 1955.*
Contribution from the Radio Physics Laboratory, Defence Research Board, Ottawa, Canada, and the U.S. Bureau of Standards, Boulder, Colorado.
The bulk of this work was carried out in Radio Physics Laboratory, Defence Research Board, Ottawa, Ontario.
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expressions for the field components can be generalized to include other angles. He justifies the extension to the case where the corner reflector angle is 2π by a comparison of his results with Sommerfeld's classical solution for diffraction of a plane wave by a conducting half-plane. By heuristic considerations and an application of Babinet's principle, Johnson then transforms the solution for the electric current element at the edge of the sheet to the notch in the edge of the complementary sheet.

In view of the rather surprising properties of the "notch" located at the edges of conducting sheets, it seems worth while to outline a rigorous derivation for the radiated fields for the case of the half-plane and the ribbon. The principal radiation patterns and the conductance of the "notches" are then computed.

NOTCH AT EDGE OF HALF-PLANE

In a previous paper (6), general expressions were given for the fields of a distribution of magnetic current in the presence of a cylindrically tipped wedge of arbitrary angle. The fields of the notch are essentially equivalent to the special case when the wedge angle is 2π and the radius of the cylindrical tip is zero. Choosing a cylindrical coordinate system (ρ, Φ, z), the surfaces of the half-plane are defined by $\Phi = 0$ and 2π. An element of magnetic current density $\mathbf{J}^*(r')$ and one of magnetic charge density $\rho^*(r')$ are located at the point Q whose coordinates are (ρ', Φ', z'). r' is a vector directed from the origin to the point Q.

Following the previous analysis, the axial components of the electric and magnetic field, in a volume V containing all the sources, can be expressed by

$$[1] \qquad E_z(r) = -\int_V [\mathbf{J}^*(r') X \nabla' G_1(r, r')]_z \, dv',$$

$$[2] \qquad H_z(r) = \int_V \left[-i\epsilon\omega \mathbf{J}^*(r') G_2(r, r') + \frac{1}{\mu} \rho^*(r') \nabla' G_2(r, r') \right]_z dv',$$

where r is a vector directed from the origin to the field point and ϵ and μ are the dielectric constant and magnetic permeability of free space. The gradient operator ∇' involves differentiation with respect to the primed coordinates. The Green's functions $G_1(r, r')$ and $G_2(r, r')$ satisfy the inhomogeneous Helmholtz equation

$$[3] \qquad (\nabla^2 + k^2) \, G_1(r, r') = -\delta(r - r')$$

where $k = 2\pi/\lambda$, λ = free space wavelength, and where $\delta(r-r')$ is the three-dimensional Dirac function. The Green's functions are subject to the following boundary conditions: $G_1(r, r') = 0$ at $\Phi = 0$ and 2π and $\partial G_1(r, r')/\partial \Phi'$

$= 0$ at $\Phi = 0$ and 2π. Again utilizing the results of the previous analysis, it follows that for the far field region such that $k\rho \gg 1$:

$$[4] \qquad G_1(r, r') = \frac{\exp[-ik(R - z'\cos\theta)]}{2\pi R} \sum_{m=1,2,3\ldots}^{\infty} \sin \nu\Phi \sin \nu\Phi' \times \exp(i\nu\pi/2) J_\nu(k\rho' \sin\theta)$$

and

$$[5] \qquad G_2(r, r') = \frac{\exp[-ik(R - z'\cos\theta)]}{2\pi R} \sum_{m=0,1,2,3\ldots}^{\infty} (\epsilon_m/2) \cos \nu\Phi \cos \nu\Phi' \times \exp(i\nu\pi/2) J_\nu(k\rho' \sin\theta)$$

where $R = (\rho^2 + z^2)^{\frac{1}{2}}$, $\theta = \tan^{-1}(\rho/z)$, J_ν is the Bessel function of the first type, and for the half-plane, $\nu = m/2$.

The source is now considered to be specifically a line element of magnetic current $K(\rho')$ directed radially at $\Phi' = \Phi_0$ from $\rho' = \rho_1$ to ρ_2 and contained in the plane $z' = 0$. The volume integrations indicated in equations [1] and [2] are now reduced to a one-dimensional integration with respect to ρ' so that

$$[6] \qquad E_z(r) = \int_{\rho_1}^{\rho_2} K(\rho') \frac{\partial G_1(r, r')}{\rho' \partial \Phi'} d\rho',$$

$$[7] \qquad H_z(r) = \frac{1}{i\mu\omega} \int_{\rho_1}^{\rho_2} K(\rho') \frac{\partial^2 G_2(r, r')}{\partial z' \partial \rho'} d\rho',$$

where the continuity equation, $\mathbf{J}^*(r') + i\omega\rho^*(r') = 0$, has been utilized. In terms of spherical coordinates (R, θ, Φ), the radiation or far fields are then

$$[8] \qquad H_\theta = \frac{-i\epsilon\omega e^{-ikR}\cos\theta}{2\pi R} \int_{\rho_1}^{\rho_2} K(\rho') \sum_{m=0}^{\infty} i^{\frac{1}{2}m-1} (\epsilon_m/2) \cos \nu\Phi \cos \nu\Phi_0 \times J_\nu'(u\rho' \sin\theta)\, d\rho',$$

$$[9] \qquad E_\Phi \simeq (-\mu\omega/k)\, H_\theta,$$

$$[10] \qquad H_\Phi \simeq \frac{i\epsilon\omega e^{-ikR}}{2\pi R} \int_{\rho_1}^{\rho_2} K(\rho') \sum_{m=1}^{\infty} i^{\frac{1}{2}m-1} \left(\frac{\nu}{k\rho' \sin\theta}\right) \sin \nu\Phi \cos \nu\Phi_0\, J_\nu(u\rho' \sin\theta)\, d\rho',$$

and

$$[11] \qquad E_\theta \simeq (\mu\omega/k)\, H_\Phi.$$

A slot on the half-plane is now considered by letting the magnetic current element approach the surface of the wedge. By the equivalence theorem (3), the magnetic current $K(\rho')$ can be identified with the voltage $V(\rho')$ across a narrow slot extending from $\rho = \rho_1$ to ρ_2. The notch can be considered as a slot on both sides of the half-plane extending from $\rho = 0$ to L as indicated in Fig. 1*a*. $K(\rho')\cos \nu\Phi_0$ in equations [8] and [10] should then be replaced by

$V(\rho')(1 + \cos m\pi)$ with $\rho_1 = 0$ and $\rho_2 = L$. The radiation fields of the "notch" are then

$$[12] \qquad E_\Phi = \frac{ke^{-ikR}\cos\theta}{\pi R}\int_0^L V(\rho')\sum_{m=1,3,5\ldots}^{\infty} i^{\frac{1}{2}m-1}\cos\tfrac{1}{2}m\Phi\, J'_{m/2}(k\rho'\sin\theta)\, d\rho'$$

and

$$[13] \qquad E_\theta = \frac{ke^{-ikR}}{\pi R}\int_0^L V(\rho')\sum_{m=1,3,5\ldots}^{\infty} i^{\frac{1}{2}m}\sin\tfrac{1}{2}m\Phi\, J_{m/2}(k\rho'\sin\theta)\left[\frac{(m/2)}{k\rho'\sin\theta}\right] d\rho'$$

where the summation in each case is over the odd values of m only.

When the voltage distribution $V(\rho')$ across the "notch" is specified, the above formulas are quite suitable for computation so long as L is less than a wavelength or so since then the series converges very rapidly. In fact if L is small compared to the wavelength, it is reasonable to assume that $V(\rho')$ varies in a linear manner from the value V_0 at the mouth of the notch ($\rho' = 0$) to zero at the base of the notch ($\rho' = L$). To this approximation the fields of the short notch are

$$[14] \qquad E_\Phi \simeq -(iL/\lambda)^{\frac{1}{2}}\, 4e^{-ikR}\, V_0\cos\theta(\sin\theta)^{-\frac{1}{2}}\cos(\Phi/2)/3\pi R$$

and

$$[15] \qquad E_\theta \simeq -(iL/\lambda)^{\frac{1}{2}}\, 4e^{-ikR}\, V_0(\sin\theta)^{-\frac{1}{2}}\sin(\Phi/2)/3\pi R$$

where the neglected terms are of order $(L/\lambda)^{3/2}$, $(L/\lambda)^{5/2}$, etc.

The power P radiated from the notch can be obtained by integrating the real part of the Poynting vector over an infinite spherical surface; this leads to

$$[16] \qquad P = \frac{1}{240\pi}\lim_{R\to\infty}\int_{\theta=0}^{\pi}\int_{\Phi=0}^{2\pi}[|E_\theta|^2 + |E_\Phi|^2]\, R^2\sin\theta\, d\theta\, d\Phi.$$

The radiation conductance of the notch referred to the voltage V_0 across the mouth is then given by

$$[17] \qquad G = 2P/V_0^2 = L/45\pi\lambda$$

subject of course to the restriction that $L \ll \lambda$. The neglected terms are of order $(L/\lambda)^3$, $(L/\lambda)^5$, etc.

This simple expression for the conductance agrees essentially with Johnson (2), except that he called the reciprocal of G, the radiation resistance of the notch. This would not be true in general since the reactance of a short notch is expected to be large.

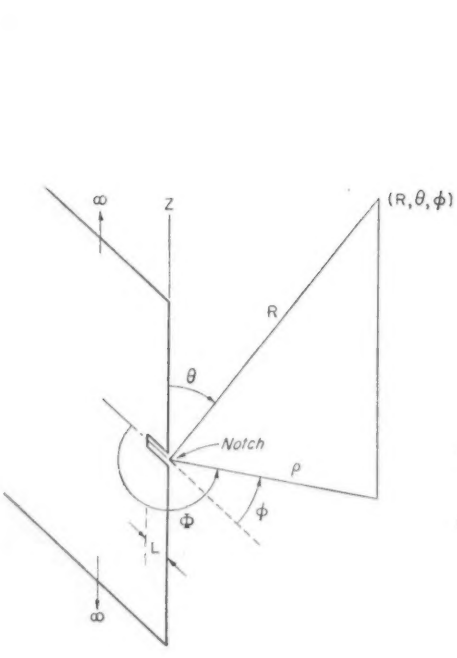
Before discussing the numerical significance of the fields of the notch on the edge of the half-plane, it is considered desirable to derive expressions for the fields of a notch on the edge of a ribbon. This will be done in the next section.

NOTCH AT EDGE OF RIBBON

When the conducting surface is in the form of a sheet or a plate, it is reasonable to expect that an elliptic cylinder is a good representation if the eccentricity is large. In a previous paper (5), a derivation was given for the electromagnetic field produced by an arbitrary slot cut in the surface of an elliptic cylinder of perfect conductivity and infinite length. The electric field tangential to the slot was assumed to be a prescribed function. When the results were specialized to the far zone region and to short axial or transverse slots, agreement was obtained with the earlier results of Wong (8), who employed a different method. In this section, the notch on the edge of a ribbon will be considered as a special case of the arbitrary slot on the elliptic cylinder.

The perfectly conducting cylinder illustrated in Fig. 1*b* is taken to be of infinite length with major axis $2a$ and minor axis $2b$. If the cylinder axis is coincident with the z axis of a rectangular coordinate system (x, y, z), the surface of the cylinder is specified by

$$x^2/a^2 + y^2/b^2 = 1. \tag{18}$$



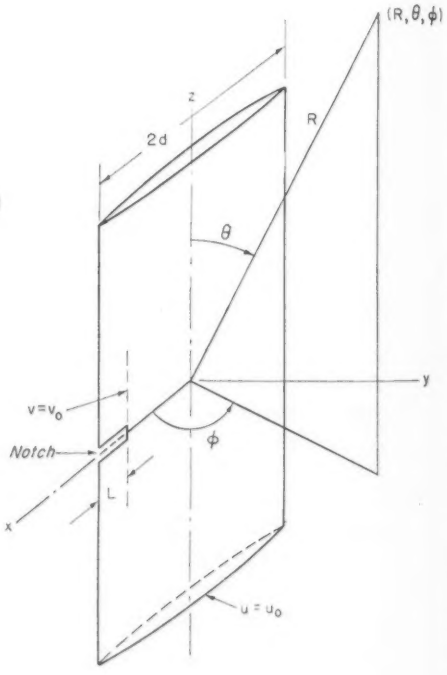


FIG. 1*a*. The notch at the edge of a conducting half-plane.
FIG. 1*b*. The notch at the edge of a conducting ribbon.

As in the previous paper, it is convenient to introduce elliptic coordinates (u, v, z) which are defined by the following transformation:

$$\begin{aligned} x &= d \cosh u \cos v, \\ y &= d \sinh u \sin v, \\ z &= z, \end{aligned} \tag{19}$$

where $2d$ is the distance between foci of the ellipse. The foci are located at the points $(x = \pm d,\ y = 0)$. The surfaces $u =$ constant represent a family of confocal cylinders of elliptic cross section. The semimajor and semiminor axes of the ellipse, $u = u_0$, are given by

$$\begin{aligned} a &= d \cosh u_0, \\ b &= d \sinh u_0. \end{aligned} \tag{20}$$

A narrow slot is located on the cylinder, $u = u_0$, at $z = 0$ extending from $v = -v_0$ to $v = +v_0$. As a result of the assumed small width of the slot, only the axial voltage $V(v)$ along the slot contributes to the fields and furthermore $V(v)$ is considered to be an even function of v. With reference to spherical coordinates (R, θ, ϕ) centered at the origin of (x, y, z) system, the far fields are given by

$$E_\theta = \frac{-iV_0 e^{-ikR}}{R \sin \theta} \left(\frac{2}{\pi} \right)^{\frac{1}{2}} \sum_{m=0}^{\infty} \frac{i^m Se_m(c, \cos \phi)}{N_m^e He_m^{(2)}(c, \cosh u_0)} Ie_m(v_0) \tag{21}$$

with

$$Ie_m(v_0) = \int_0^{v_0} V(v) Se_m(c, \cos v)\, dv$$

and

$$E_\phi = \frac{iV_0 e^{-ikR}}{R \sin \theta} \left(\frac{2}{\pi} \right)^{\frac{1}{2}} \cos \theta \sum_{m=1}^{\infty} \frac{i^m So_m(c, \cos \phi)}{N_m^o \left[\partial Ho_m^{(2)}(c, \cosh u) / \partial u \right]_{u=u_0}} Io_m(v_0) \tag{22}$$

with

$$Io_m(v_0) = \int_0^{v_0} V(v) \frac{\partial}{\partial v} So_m(c, \cos v)\, dv,$$

where $c = kd \sin \theta$. The functions $He_m^{(2)}$ and $Ho_m^{(2)}$ are the radial Mathieu functions of the even and odd type respectively, whereas Se_m and So_m are the corresponding angular functions. N_m^e and N_m^o are the even and odd normalization constants.

The limiting case of a very thin elliptic cylinder or ribbon of width $2d$ is obtained by setting $u_0 = 0$ and $\cosh u_0 = 1$ in equations [21] and [22]. Using available tables of Mathieu functions (4), the above formulae can be used to calculate the fields having specified the functional form for $V(v)$. Considering the notch to be again of depth L, the elliptic coordinate v_0 is given by

$$\cos v_0 = 1 - L/d \tag{23}$$

and if the voltage $V(v)$ is assumed to be a linear function of distance from the value V_0 at the mouth of the slot, it follows that

$$V(v) = V_0 \left[\frac{\cos v - \cos v_0}{1 - \cos v_0} \right] \text{ for } 0 \leqslant |v| < v_0 \tag{24}$$

and $V(v) = 0$ for $v > v_0$. It is now noted that

$$[25] \qquad Se_m(c, \cos v) = \sum_{n=0}^{\infty}{}' De_n^m \cos nv$$

and

$$[26] \qquad So_m(c, \cos v) = \sum_{n=0}^{\infty}{}' Do_n^m \sin nv$$

where the prime indicates summation over even (odd) values of n if m is even (odd) and the coefficients are tabulated in the Columbia tables (4). The integration with respect to v indicated in equations [21] and [22] can now be carried out to yield

$$[27] \quad Ie_m(v_0) = \frac{1}{1-\cos v_0} \sum_{n=0}^{\infty} De'_m \left[\frac{\sin(1-n)v_0}{2(1-n)} + \frac{\sin(1+n)v_0}{2(1+n)} - \frac{\cos v_0 \sin nv_0}{n} \right],$$

$$[28] \quad Io_m(v_0) = \frac{1}{1-\cos v_0} \sum_{n=1}^{\infty} Do'_m \left[\frac{\sin(1-n)v_0}{2(1-n)} + \frac{\sin(1+n)v_0}{2(1+n)} - \frac{\cos v_0 \sin nv_0}{n} \right] n.$$

When $L \ll \lambda$ the above expressions simplify considerably to

$$Ie_m(v_0) \simeq Io_m(v_0) \simeq \tfrac{2}{3} v_0 \simeq \tfrac{2}{3}(2L/d)^{\frac{1}{2}}$$

where the neglected terms are of order $(L/d)^{3/2}$, $(L/d)^{5/2}$, etc.

The conductance for the notch on the ribbon is obtained from

$$[29] \qquad G = \frac{1}{120\pi V_0^2} \int_0^{2\pi} \int_0^{\pi} [|E_\theta|^2 + |E_\phi|^2] R^2 \sin\theta \, d\theta \, d\phi.$$

Utilizing the orthogonality properties of the angular Mathieu functions, it follows that

$$[30] \quad G = \frac{1}{30\pi^2} \int_0^{\pi/2} \frac{1}{\sin\theta} \left[\sum_{m=0}^{\infty} \frac{[Ie_m(v_0)]^2}{N_m^e \, |He_m^{(2)}(c, 1)|^2} + \sum_{m=1}^{\infty} \frac{\cos^2\theta [Io_m(v_0)]^2}{N_m^o \, |Ho_m^{(2)\prime}(c, 1)|^2} \right] d\theta$$

where $$Ho'_m(c, 1) = [\partial Ho_m(c, \cosh u)/\partial u]_{u=0}.$$

PRESENTATION OF CALCULATED RESULTS

It can be seen from equations [21] and [22] that the radiated fields are elliptically polarized for both the notch on the half-plane and that on the ribbon. In the principal planes (i.e. $\theta = 90°$ and $\phi = 0°$, 180°), the E_Φ component of the field vanishes and the field becomes plane polarized. For purposes of presentation of the principal patterns, the quantity that is calculated is

$$[31] \qquad P_\theta = \left(\frac{\pi}{2} \right)^{\frac{1}{2}} \frac{R}{V_0} |E_\theta|$$

which, of course, is dimensionless.

The pattern P_θ in the equatorial plane ($\theta = 90°$) is plotted in Figs. 2*a*, 2*b*, and 2*c* as a function of ϕ for $kd = 2$, 4, and 8 respectively, for $L = \lambda/20$. Since L, the depth of the notch, is small compared to λ, the approximate

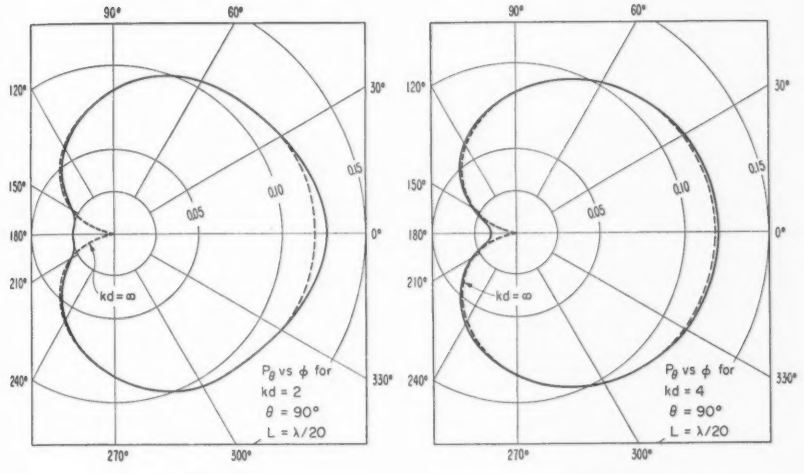


Fig. 2a

Fig. 2b

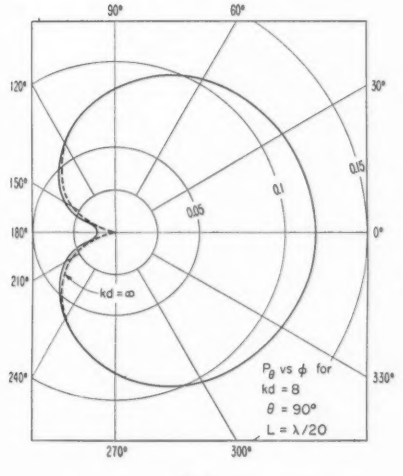


Fig. 2c

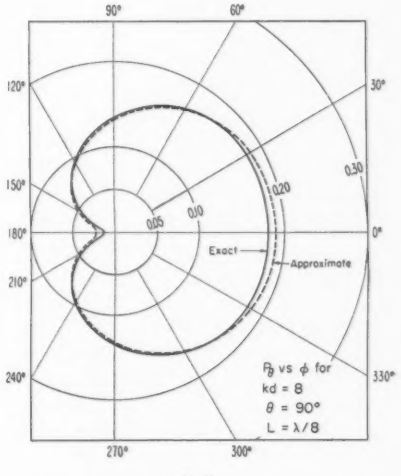


Fig. 3

FIG. 2*a*, *b*, *c*. The azimuthal radiation pattern in the principal plane ($z = 0$) for a short ($\lambda/20$) notch at the edge of a ribbon of width $2d$.

FIG. 3. The azimuthal radiation pattern in the principal plane ($z = 0$) for a short ($\lambda/8$) notch at the edge of a ribbon of width $2d$.

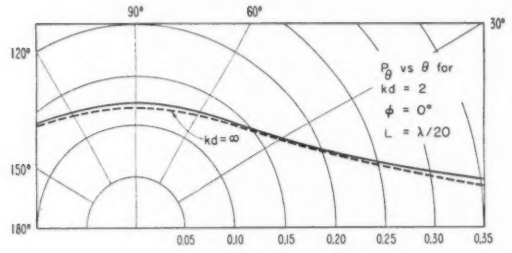


Fig. 4

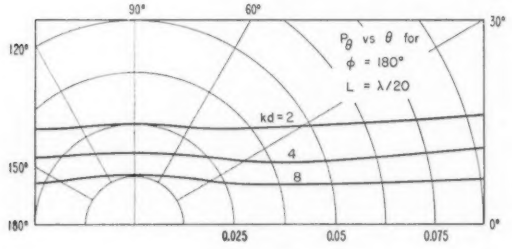


Fig. 5

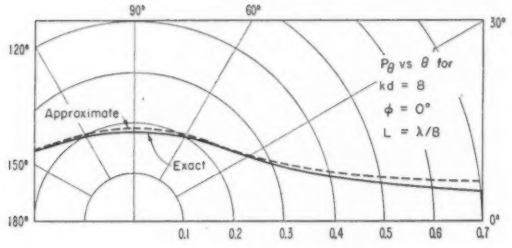


Fig. 6

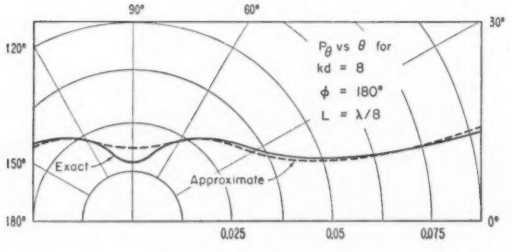


Fig. 7

FIG. 4. The principal elevation pattern in the plane $\phi = 0$ for a short ($\lambda/20$) notch.
FIG. 5. The principal elevation pattern in the plane $\phi = 180°$ for a short ($\lambda/20$) notch.
FIG. 6. The principal elevation pattern in the plane $\phi = 0$ for a short ($\lambda/8$) notch.
FIG. 7. The principal elevation pattern in the plane $\phi = 180°$ for a short ($\lambda/8$) notch.

formulas for Ie_m and Io_m are used. The corresponding patterns for the half-plane ($kd \to \infty$) are also indicated in Fig. 2 where $\phi = \Phi - \pi$. It is interesting to note the similarity of the patterns between the ribbon and the half-plane. The only essential difference is that the field at $\phi = 180°$ to the rear of the notch is finite for the ribbon but identically zero for the half-plane.

The equatorial plane pattern ($\theta = 90°$) for the notch of length $L = \lambda/8$ is shown in Fig. 3 for the two cases where the exact and the approximate representations for Ie_m and Io_m are employed. The close resemblance between these curves justifies the use of the simple form for Ie_m and Io_m if $L \leqslant \lambda/8$.

The principal elevation pattern ($\phi = 0$) is shown plotted in Fig. 4 as a function of θ for a short notch ($L = \lambda/20$) for the cases $kd = 2$ and $kd = \infty$. The curves for cases $kd = 2$ and 4 were also computed, but they are not shown since they were between the $kd = 2$ and ∞ curves. The corresponding elevation pattern for the short notch in the plane $\phi = 180°$ is plotted in Fig. 5 for $kd = 2$, 4, and 8. Of course, the pattern function P_θ for $\phi = 180°$ for $kd = \infty$ would be identically zero and is, therefore, not plotted.

The elevation patterns for $kd = 8$ and $\lambda/8$ notch are shown in Figs. 6 and 7 using both the exact and approximate representations for Ie_m and Io_m.

It is noted that the elevation patterns for both the half-plane and the ribbon appear to be approaching infinity as θ tends to zero. In the case of the half-plane, this is due to the presence of the $(\sin\theta)^{\frac{1}{2}}$ term in the denominator.

The conductance $G(kd)$ of the short notch on the edge of the ribbon is given by equation [30] as a function of kd. The integrations were carried out by numerical methods and $G(kd)$ is shown plotted in Fig. 8 expressed as a ratio to $G(\infty)$ $[=L/45\pi\lambda]$, the conductance of the notch at the edge of the half-plane. It is observed that the ratio is only a few per cent greater than unity and appears to be asymptotically approaching unity for large values of kd.

It is significant to note that although the electric field radial to the edges of the ribbon and half-plane approaches infinity, the integrated Poynting flux is finite. From the mathematical standpoint, however, there might be some question in the reader's mind as to the validity of using the saddle point approximated fields for a narrow cone about the z axis. It can be shown,

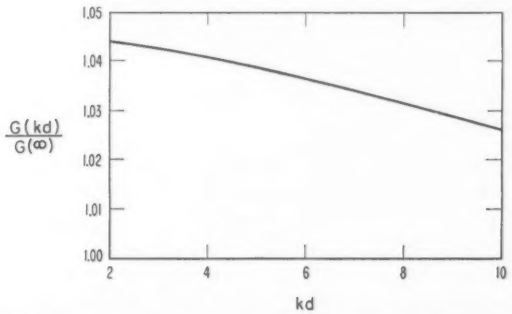


FIG. 8. The ratio of the radiation conductance $G(kd)$ for the notch on a ribbon of width $2d$ to the radiation conductance $G(\infty)$ for the notch on a half-plane.

however, that the contribution from this cone of invalidity to the energy flux integration is negligible. At the suggestion of one of the authors (J.R.W.), Dr. Frank Northover has obtained alternative expansions for the far fields which are essentially suitable for large values of z and small distances from the edge. His work, which is being submitted to the Canadian Journal of Physics, supports the contention that negligible error is introduced when the saddle point fields are employed in the energy flux integration.

CONCLUDING REMARKS

The analyses presented in this paper would indicate that radiated fields of a short notch of length L at the edge of a large conducting sheet are closely proportional to $(L/\lambda)^{\frac{1}{2}}$ for a constant voltage at the notch. Furthermore, the conductance varies almost directly with L/λ. The effect of the finite width $2d$ of the metal sheet or ribbon is very slight as long as $2d > \lambda$. The effect of length is not as easy to determine although the curves in Part I (7) for the conductance of an axial slot at the center of the ribbon would indicate that the ribbon is effectively infinite if an edge parallel to the slot or notch is at least one wavelength away in distance.

ACKNOWLEDGMENT

We would like to express our appreciation to Mrs. Anabeth Murphy who carried out the conductance calculation, and to Dr. J. Y. Wong and Dr. R. C. Langille for their helpful comments and interest shown.

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HYDROLYSIS OF CELLULOSE ACETATE SULPHATE IN ACETONE/WATER SOLUTIONS[1]

By Paul E. Gagnon, Karl F. Keirstead,[2] Jessie Walker,[3] and Keith R. Kavanaugh[3]

ABSTRACT

The kinetics of the hydrolysis of the sulphate ester of cellulose acetate sulphate in acetone/water solutions have been studied. The reaction was not diffusion controlled nor was it heterogeneous. An increase in water concentration markedly decreased the rate of hydrolysis. The rate of appearance of sulphuric acid has been found to be essentially first order over a water concentration range of 0.27 to 1.67 moles per liter (i.e. 0.5 to 3.0% vol.). Ethanol and methanol were found to have the same inhibiting effect while benzene had no effect on the reaction rate. An increase in temperature and a decrease in water concentration resulted in a decrease in the activation energy. The kinetics of the hydrolysis of various salts of cellulose acetate sulphate have also been studied.

INTRODUCTION

A previous report (3) showed that the rate of the hydrolysis of the sulphate ester of cellulose acetate sulphate depended on various factors of which the liquid medium was considered the most important. In acetone solution the hydrolysis of the sulphate ester was rapid and was influenced by the water content of the acetone. The object of the present work was to study the kinetics of this reaction.

Malm *et al.* (4) have shown that when the cellulose acetate sulphate is dissolved in acetic acid and reprecipitated with water, the sulphate content is practically unchanged. It is reduced to about 0.05% when acetone is used as the solvent. They assume an ester of the form RSO_4H. Araki and Tadenuma (1) have studied the behavior of the sulphate radical of cellulose acetate sulphate in mixed organic solvents: acetone/water, acetone/alcohol, acetone/benzene, and others. They showed that the addition of water and alcohol to acetone markedly decreased the amount of sulphate radical split off in 24 hr. while benzene had very little effect. In water the cleavage of the acetate ester is more rapid than the decomposition of the sulphate ester (2). The solvent or non-solvent medium seems to have a marked effect on the rate of solvolysis of the sulphate ester of a cellulose mixed ester.

EXPERIMENTAL

Materials

Cellulose acetate sulphate was prepared from high grade cotton linters supplied by the Hercules Powder Co., using the method reported by Keirstead and Myers (2).

[1]*Manuscript received in original form July 21, 1955, and as revised, November 25, 1955. Contribution from the Department of Chemistry, Laval University, Quebec, Quebec, with financial assistance from the Defence Research Board of Canada.*

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Reagent grade acetone was used and was analyzed for water content by an "infra-red" absorption method.

The cellulose acetate sulphate was washed continuously with distilled water passed through an ion exchange column to prevent the build-up of free acid and to eliminate the possibility of ion exchange with cellulose acetate sulphate. This free acid would have increased the rate of decomposition. Analysis of effluent water verified the efficiency of the ion exchange column.

Salts of cellulose acetate sulphate were prepared by covering the samples with 0.01 *N* solution of sodium, potassium, calcium, or magnesium chloride and allowing it to stand for 10 min. This was repeated at least three times. Each sample was given three rapid washes with distilled water and then dried by centrifuging to approximately 40% moisture content. It should be noted that great care must be taken in washing the sodium salt since the sodium is easily replaced by the hydrogen ion.

Solvolysis

A sample of cellulose acetate sulphate was removed from the washing apparatus and dried to about 40% water content by centrifuging for 10 to 15 min. Samples were set aside for moisture and gravimetric sulphate determinations (2). The initial concentration of sulphate ester was determined titrimetrically by dissolving 1 gm. of the cellulose acetate sulphate in 100 ml. of 90% acetone and immediately diluting the solution to 200 ml. of 70% acetone. Cellulose acetate sulphate solutions of varying concentrations were prepared in various acetone/water mixtures. They were immediately placed in a constant temperature bath controlled to $\pm 0.1^\circ$ C. The starting time of the experiment was taken when half the solvent had been added to the ester. Aliquots were removed from the solutions at intervals and the reaction stopped by dilution to 200 ml. of 70% acetone. The increase in acidity was measured by titration with 0.01 *N* sodium hydroxide solution as described below. Since the cellulose acetate sulphate decomposed very rapidly when dry, it was necessary to keep the interval between drying and addition to the acetone/water to a minimum.

The milliequivalents of sulphuric acid per 100 gm. sample was calculated from the following formula:

$$\text{meq. } H_2SO_4/100 \text{ gm. CAS} = \frac{\text{titer at pH } 5.35 \times N \times 100}{\text{sample wt.}}.$$

The per cent hydrolysis is given by $(a/x) \times 100$ where "a" represents the number of millimoles of sulphate ester RSO_4H which have been converted to sulphuric acid and "x" represents the number of millimoles of sulphate ester in 100 gm. of original sample $RSO_4H + H_2O = ROH + H_2SO_4$. Since the cellulose acetate sulphate remains in the solution being titrated, the mixture contains $x - a$ millimoles of RSO_4H plus a millimoles of sulphuric acid which on titration requires $x - a + 2a = x + a$ milliequivalents of sodium hydroxide.

The salts of the cellulose acetate sulphate were hydrolyzed as described above and the acid liberated was titrated by the method reported previ-

ously (2). Sodium and calcium chlorides were found to have very little effect on the titrimetric analysis.

Analytical Methods

The acidity of the solutions increased during hydrolysis owing to the formation of both sulphuric and acetic acids. The method used for determining sulphuric acid in the presence of acetic acid was based on that described by Keirstead and Myers (2). The ionization of acetic acid was sufficiently depressed in a 70% acetone/30% water solution to allow separation of the two acids. Known mixtures of dilute sulphuric acid and acetic acid in 200 ml. of 70% acetone were titrated with 0.01 *N* sodium hydroxide using a Macbeth pH meter. A marked inflection occurred in the curves at a pH of 5.25 to 5.50. At a pH of 5.35 all the sulphuric acid was titrated to within ±6% for solutions containing less than 70% acetic acid and with the concentration of total acid ranging from 0.20 to 0.40 milliequivalents. Outside these limits the method was not as accurate.

To test the accuracy of the method in the presence of cellulose acetate sulphate, known concentrations of sulphuric and acetic acids and mixtures of these two were added to 200 ml. of 70% acetone/30% water solution containing the same amount of cellulose acetate sulphate. The solutions were titrated with 0.01 *N* sodium hydroxide solution. The total volumes of 200 ml. or more were necessary to minimize the errors introduced by the lowering of the acetone concentrations on the additions of the standard alkaline solutions. The results thus obtained showed that for cellulose acetate sulphate samples containing 20.2 meq. of sulphuric acid, the maximum deviation for the total sulphate content due to the addition of 4.0 meq. of acetic acid or less was 1.9%.

The dilution of cellulose acetate sulphate solutions to 70% acetone/30% water effectively stopped the hydrolysis of sulphate esters. Those solutions in 70% acetone which were left standing for five hours showed no increase in sulphuric acid concentration although the acetic acid concentration had increased. No independent method of checking this procedure was found. The difficulty was due mainly to the cellulose acetate sample which did not precipitate from acetone solution until the solution was at least three days old, regardless of the amount of water added. Even after three days, the precipitates tended to be gelatinous and difficult to filter.

The initial concentrations of sulphate ester determined titrimetrically were found to be consistently lower than the gravimetric sulphate values. The method of preparing the solutions for determination of initial concentration of sulphate ester had no apparent effect on the values. Solutions were prepared by dissolving the cellulose acetate sulphate sample in 100 ml. of 99, 97, 95, 93, and 90% acetone and immediately diluting the solution to 200 ml. of 70% acetone. The 90% acetone was preferable because hydrolysis in this solvent was very slow. This allowed more time for the preparation of solutions and prevented the formation of sulphuric acid which would have increased the error in the calculation of the initial concentration of sulphate ester.

Since the initial concentrations of sulphate esters determined titrimetrically were consistently lower than the gravimetric sulphate values, indications were that either the sulphate was present as acid ester and neutral ester or that some salt formation had occurred with stray sodium, potassium, calcium, or copper ions in the wash water. The gravimetric and titrimetric values were compared with the "apparent" sulphate value determined from the maximum hydrolysis value for each cellulose acetate sulphate. The "apparent" sulphate and titrimetric sulphate values showed the greatest degree of correlation as indicated by the coefficients of correlation given below:

	Coefficient of correlation
"Apparent" and titrimetric sulphate	0.983
Gravimetric and "apparent" sulphate	0.952
Gravimetric and titrimetric sulphate	0.943

These results supported the idea that the sulphate was present as acid ester and neutral ester, assuming that the acid ester hydrolyzed very rapidly while the neutral ester was quite stable. If the difference between the two sulphate values had been due to salt formation, the gravimetric and apparent sulphate values should have shown the greatest degree of correlation because the salts of cellulose acetate sulphate hydrolyzed very rapidly in the presence of acid ester (at a rate approximating that of the acid ester).

The titrimetric sulphate values were used for all calculations, and values greater than 100% for hydrolysis were taken to indicate that some neutral ester had hydrolyzed.

Experiments done on any given day using the same sample were reproducible to within ±5%. Experiments with the same sample on two successive days were fairly reproducible although there was a tendency for the rate of hydrolysis to decrease with the age of the sample. A marked decrease in the rate of hydrolysis was noted when experiments were run on the same sample three or four days apart. This decrease in rate of hydrolysis with age must be the result of the decrease in acetate concentration in the cellulose acetate sulphate since the sulphate concentration remained practically constant (2).

RESULTS AND DISCUSSION

The rate of hydrolysis varied markedly from one sample to another as shown in Fig. 1. There was an indication that the rate of hydrolysis decreased with decreasing acetyl concentration, but it is not conclusive since the acetyl results were not very accurate. The rate of stirring of the sample and the addition of glass wool or beads to the reaction flasks did not affect the rate of hydrolysis. It may be concluded that the reaction is not diffusion controlled nor is it heterogeneous.

The concentration of water in acetone had a marked effect on the rate of hydrolysis. As the water concentration increased, the rate of hydrolysis decreased rapidly until the water concentration reached 3% by volume. Thereafter the effect was not as marked. Results for the hydrolysis of two different

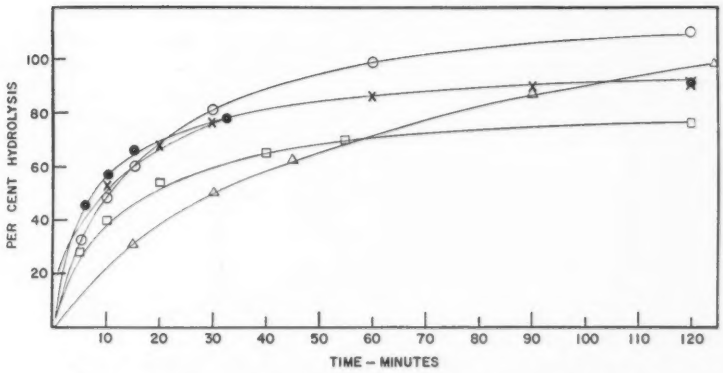

FIG. 1. Hydrolysis of various samples of cellulose acetate sulphate.

		Sulphuric acid		
		Grav. meq./100 gm.	Titrimetric meq./100 gm.	H_2O conc., % vol.
×	CA 101—2nd day	30.9	24.7	0.63
●	114—2nd day	30.5	28.6	0.66
△	99—3rd day	27.9	25.5	0.70
□	89—3rd day	26.8	24.3	0.84
○	106—1st day	43.7	33.3	0.74

samples at a temperature of 35.5° C. are plotted in Fig. 2. The rate constants used were first order because the concentration of water was approximately 150 times greater than the concentration of sulphate on a molar basis for the lowest water concentration obtainable. Similar results were obtained at 25° C. and 18.8° C.

The addition of methanol and ethanol to acetone reduced the rate of hydrolysis as shown by Table I. Benzene had no appreciable effect on the reaction as shown in Fig. 3.

Sulphuric and acetic acids had no appreciable effect on the rate of the reaction over the concentration range studied, as indicated in Table II. The results are expressed as milliequivalents of sulphuric acid present in the

TABLE I

EFFECT OF METHANOL AND ETHANOL CONCENTRATION ON HYDROLYSIS

	Concentration of methanol in moles/liter					Concentration of ethanol in moles/liter				
Time, min.	0	0.124	0.248	0.496	1.24	0	0.085	0.171	0.341	0.850
	H_2SO_4 present at time indicated, meq.					H_2SO_4 present at time indicated, meq.				
20	23.3	16.2	—	—	—	17.0	14.0	—	—	—
60	25.4	21.3	19.2	14.9	8.9	21.5	20.7	17.4	14.4	—
120	26.3	21.9	20.2	16.6	10.0	23.1	22.4	—	—	—
240	27.5	22.9	21.1	16.6	10.3	23.1	22.3	20.2	17.8	13.2
360	—	23.2	21.1	16.6	10.0	23.4	23.1	20.2	—	12.4
600	—	—	23.9	19.1	10.4	—	23.4	20.1	17.3	12.9
						—	—	20.5	17.4	13.3
24 hr.	—	—	—	18.9	10.4	—	—	—	17.4	13.3

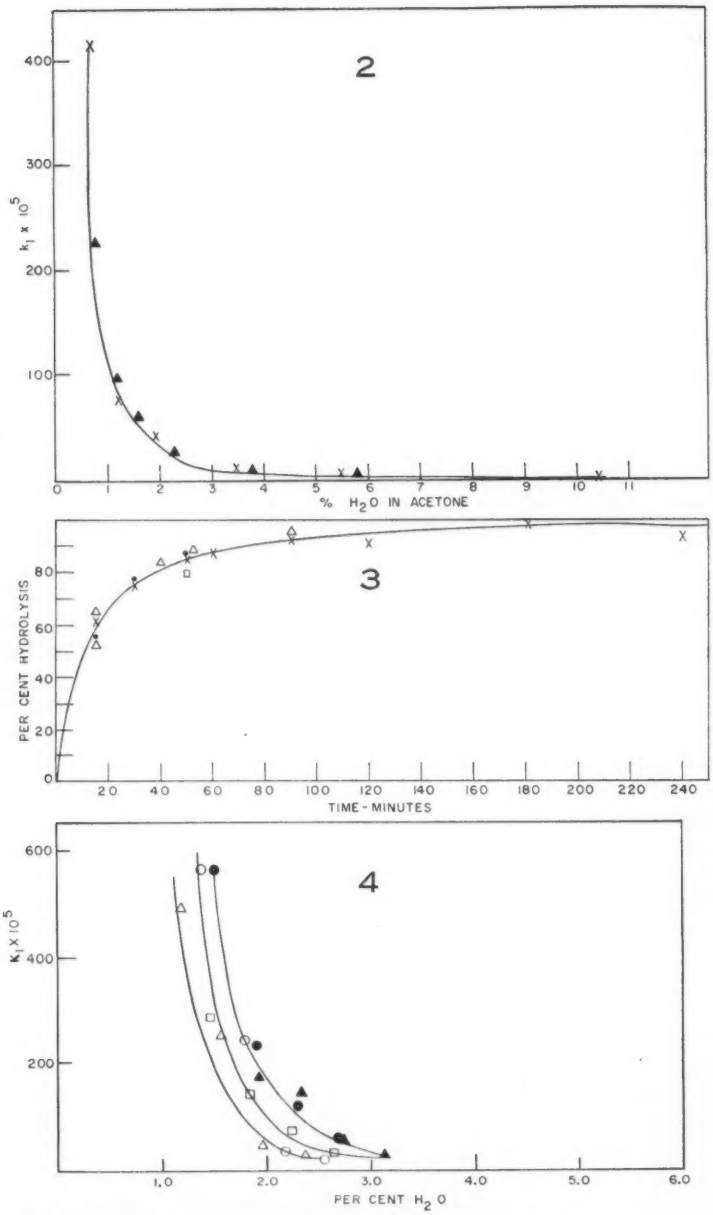

FIG. 2. Effect of water concentration on rate of hydrolysis.
× Sample CA 106—2nd day, conc. = 0.751 gm./100 ml. Temp. = 35.5° C.
▲ Sample CA 108—2nd day, conc. = 0.684 gm./100 ml. Temp. = 35.5° C.

FIG. 3. Effect of benzene concentration on rate of hydrolysis of CA 101—3rd day. Benzene concentration, % vol. = ×, 0; ●, 1.0; △, 2.5; □, 5.0.

FIG. 4. Effect of water concentration and C.A.S. concentration on rate of hydrolysis. Sample CA 110—2nd day, C.A.S. concentration, gm./100 ml. = △, 0.810; ○, 0.486; □, 1.293; ●, 1.051; ▲, 0.646. Temp. = 25° C.

TABLE II

EFFECT OF SULPHURIC ACID AND ACETIC ACID CONCENTRATIONS ON HYDROLYSIS

Time, min.	Sulphuric acid concentration, meq. 0.0N	0.00038N	0.00056N	0.00075N	0.00095N	Time, min.	Acetic acid concentration, meq. 0.0N	0.00038N	0.00056N	0.00075N	0.00095N
15	38.1	39.9	39.5	39.4	37.2	15	33.6	35.8	35.1	34.9	32.3
30	43.9	43.9	44.2	44.9	43.9	30	38.5	39.6	39.7	40.0	39.1
45	48.6	47.9	47.5	45.2	48.5	45	41.7	43.0	43.6	44.5	43.4
90	54.5	50.5	49.7	50.4	53.7	90	48.1	47.9	48.5	48.4	49.1
135	52.4	54.2	53.0	56.5	—	135	50.7	—	50.3	51.8	54.5
240	61.0	55.6	57.1	58.0	58.2	240	55.5	51.0	51.8	53.0	56.8
420	61.6	56.6	63.1	59.4	59.8	360	55.3	51.0	52.3	52.8	55.8

solution at the specified times after correction for the concentration of sulphuric acid added. The concentration of acid added had to be low to keep within the limits of the analytical method.

In Fig. 4 the first order rate constants are plotted against the water concentration for five different concentrations of cellulose acetate sulphate. Even though the experiments were done on the same day using one sample of cellulose acetate sulphate, the results were scattered, but they indicated that the rate of hydrolysis was independent of the cellulose acetate sulphate concentration. An error of 10% in the water concentration could account for the variations in rate. The total water concentration was calculated by adding the concentration of water present in the cellulose acetate sulphate sample and in the acetone to the concentration of water added for each experiment so that an error of this magnitude was possible.

The rate of hydrolysis was determined at four different water concentrations at temperatures of 24.7° C. and 35.8° C. for sample CA 106—1st day, 18.8° C. and 35.5° C. for sample CA 108—1st day, and of 19.5° C. and 25° C. for sample CA 105—2nd day. The results are given in Table III. The activation energies E_{cal} were calculated by the usual relation:

$$\log k_2/k_1 = (E/2.303\ R) \times [(T_2 - T_1)/(T_2T_1)]\,.$$

Alternatively E_{cal} was also obtained from the slope of the plot of log k against $1/T$. Since the water concentration C affects the reaction rate k, it became necessary to obtain values of k_1 and k_2 of the same water concentration. k_1 and k_2 for this selected value of C_3 were read from the plot of k_1 against C_1 and k_2 against C_2, respectively. It should be noted that the activation energy tended to increase with increasing water concentration and also to increase markedly as the temperature decreased. Errors up to 25% are possible in activation energies for errors up to 10% in water concentration. Variations in the acetyl content and sulphate ester content of the cellulose acetate sulphate samples probably affect the hydrolysis rates and may account for some of the differences in the activation energies. Hydrolysis of neutral ester should become more complete as the temperature increases.

If the reaction proceeded according to the equation $ROSO_3H + HOH =$

TABLE III

EFFECT OF TEMPERATURE ON HYDROLYSIS

Sample CA 106—1st day					
T_1 = 24.7° C.		T_2 = 35.8° C.			E_{cal} (24.7–35.8)
C_1	k_1	C_2	k_2	C_3	
0.041	1.94	0.035	2.517		
0.0634	1.83	0.057	2.262	0.0417	18,500
0.0855	1.314	0.0795	1.98	0.0695	18,650
0.113	1.176	0.108	1.713	0.111	19,450
Sample CA 108—1st day					
T_1 = 18.8° C.		T_2 = 35.5° C.			E_{cal} (18.8–35.5)
C_1	k_1	C_2	k_2	C_3	
0.0378	1.308	0.040	2.352		
0.0600	0.905	0.0411	2.615	0.0417	29,000
0.0822	0.692	0.0629	1.984	0.0695	29,800
0.104	0.324	0.0634	2.158	0.111	31,500
		0.0855	1.806		
		0.0850	1.806		
		0.108	1.505		
		0.124	1.406		
Sample CA 105—2nd day					
T_1 = 19.5° C.		T_2 = 25° C.			E_{cal} (19.5°–25°)
C_1	k_1	C_2	k_2	C_3	
0.0411	1.599	0.0816	1.634		
0.0600	1.243	0.104	1.371	0.0555	43,600
0.0605	1.230	0.126	1.086	0.0835	44,000
0.0800	0.845	0.154	0.800	0.111	45,000
0.0822	0.914				
0.0967	0.690				
0.110	0.616				

$ROH+H_2SO_4$, it was a bimolecular reaction dependent on both the sulphate ester concentration and the water concentration. The minimum concentration of water obtained in these experiments was about 0.5 gm. per gram of cellulose acetate sulphate. On a molar basis the minimum concentration of water present in any hydrolysis was approximately 150 times greater than the concentration of sulphate ester. If the above mechanism is correct, the reaction should proceed as a pseudounimolecular reaction (the water concentration remaining approximately constant during the reaction) and should follow the equation $k_1 = (2.303/t) \log[x/(x - a)]$ where x is the initial concentration of cellulose acetate sulphates and $x - a$ is the concentration after time t.

Plots of $\log[x/(x - a)]$ against t gave straight lines for water concentrations of less than 3% (Figs. 5 and 6). The lines did not always extrapolate to zero, indicating the presence of some free sulphuric acid in the cellulose acetate

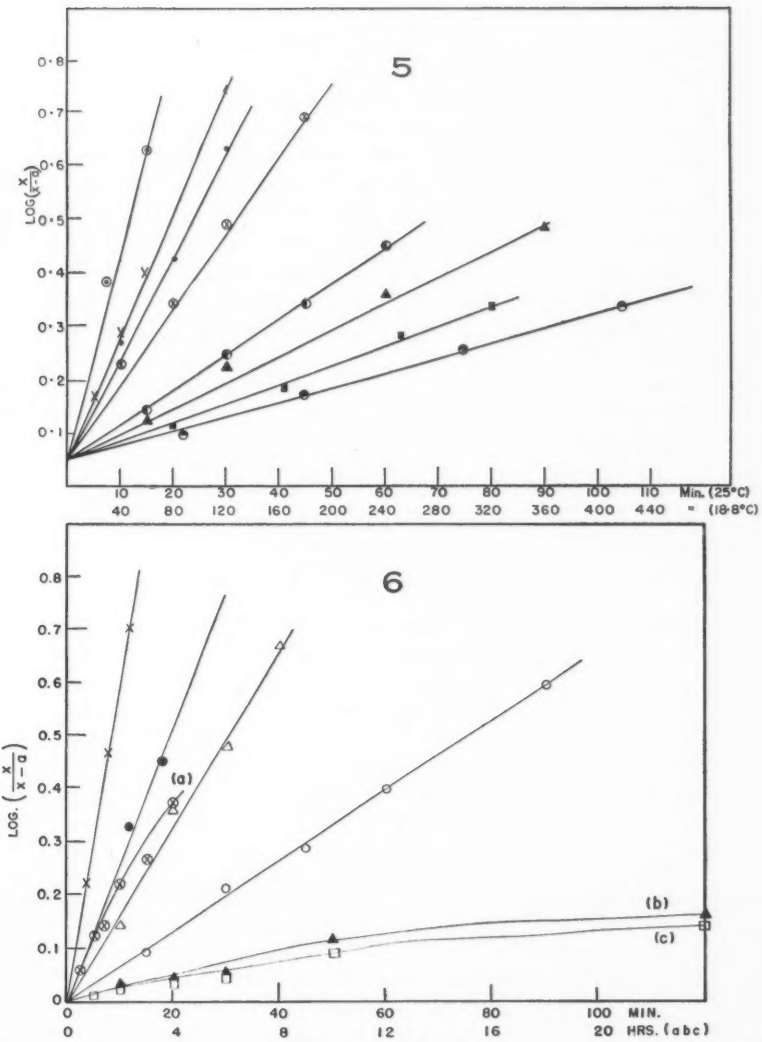

FIG. 5. Curve of $\log[x/(x-a)]$ against time. Sample CA 106—1st day, temp. = 25° C., H_2O % vol. = ×, 0.74; ●, 1.14; ▲, 1.54; ■, 2.04. Sample CA 108—1st day, temp. = 18.8° C., H_2O % vol. = ⊙, 0.68; ⊗, 1.08; ◐ ●, 1.48; ◓, 1.98.

FIG. 6. Curve of $\log[x/(x-a)]$ against time. Sample CA 108—2nd day, temp. = 35.5° C., H_2O % vol. = ×, 0.78; ●, 1.13; ⊗, 2.23; △, 1.53; ○, 3.73; ▲, 5.73; □, 10.73.

sulphate samples. Cellulose acetate sulphate decomposed in the dry fiber state and some decomposition could have occurred in the time interval used for weighing up the samples.

An increase in water concentration was found to decrease the rate of hydrolysis. An increase in the age of the cellulose acetate sulphate which caused a decrease in the acetyl content also decreased the rate of reaction. The activation energy increased with a decrease in temperature and an increase in water concentration. These effects could result from the stabilization of the sulphate ester by solvation. As the water concentration increased and the temperature decreased, the sulphate ester must have become solvated and hence splits off less readily. As the acetyl concentration decreased, the sulphate ester became more accessible for stabilization by solvation. The theory that the sulphate ester may be stabilized by solvation with water is supported by the fact that methanol and ethanol also decreased the rate of hydrolysis while benzene had no effect.

Hydrolysis of the sodium salt occurred for samples in acetone solutions containing 0.76% water at 33.0° C. and 0.81% water at 25.0° C. An inhibition period was found in both cases (Table IV). For water concentration greater

TABLE IV

HYDROLYSIS OF SODIUM SALT

Sample CA 107—2nd day Temp. = 33° C. Water conc., 0.76 ml./100 ml.		Sample CA 103—2nd day Temp. = 25° C. Water conc., 0.81 ml./100 ml.	
Time, min.	Hydrolysis, %	Time, hr.	Hydrolysis, %
15	0	0.5	0
30	0	1.0	1.7
60	4.0	2.0	32.7
90	49.9	7.0	70.1
120	78.6	6.0	87.8
180	80.9	10.0	87.8
240	92.6	24.0	87.8

than 1% no hydrolysis occurred, even after 96 hr. at 33° C. If the sodium salt was not completely neutralized, the hydrolysis proceeded at a fair rate and for water concentrations of less than 1%, it was almost complete in 24 hr. (Fig. 7). The addition of sulphuric acid increased the rate of the reaction and eliminated the inhibition period for a sample which was not completely neutralized. The addition of a trace of sulphuric acid to samples which had not hydrolyzed after 24 hr. initiated hydrolysis after a further six hours, while the addition of acetic acid to solutions of the sodium salt in concentrations 0.0005 *N*, 0.001 *N*, and 0.0015 *N* had no effect, even after 24 hr.

An attempt was made to hydrolyze the potassium salts of CA 114—2nd day at 25.0° C. in acetone solutions containing 0.63, 1.03, 1.43, and 1.83% water by volume respectively. No hydrolysis had occurred at the end of eight hours.

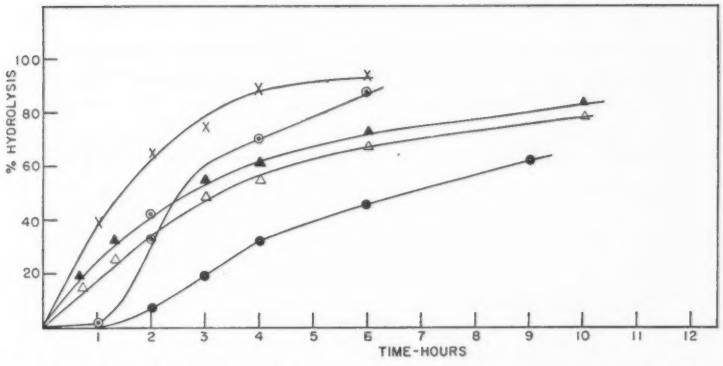

FIG. 7. Effect of sulphuric acid concentration on rate of sodium salt hydrolysis.

	H_2O conc., % vol.	H_2SO_4 conc.
Sample CA 105—1st day pH 6.55 in 70% acetone	× 0.59	
	● 1.59	
	△ 1.59	0.0005 *N*
	▲ 1.59	0.001 *N*
Sample CA 103—2nd day pH 7.35 in 70% acetone	⊙ 0.81	

A completely neutral magnesium salt was not obtained. Even after treatment of a sample of cellulose acetate sulphate nine times with a magnesium chloride solution, a 70% acetone solution of the salt had a pH of 5.00. The hydrolysis results obtained with this salt are given in Table V. There was an inhibition period for each hydrolysis which increased with increasing water concentration. The salt was completely hydrolyzed after 24 hr. for all experiments except that with 2.05% water concentration.

Calcium salts, which were not completely converted to the salt, hydrolyzed very rapidly in low water concentrations. Hydrolysis was complete after one hour in one experiment where the blank showed 4.34 meq. of sulphuric acid. The presence of acetic acid had little effect on the rate of hydrolysis.

TABLE V

HYDROLYSIS OF MAGNESIUM SALT OF CA 114—1ST DAY

Water concentration (% vol.)							
0.85		1.25		1.65		2.05	
Time, min.	Hydrolysis, %	Time, min.	Hydrolysis, %	Time, min.	Hydrolysis, %	Time, min.	Hydrolysis, %
10	0	15	0	20	0	30	0
20	0	30	0	40	0	90	0
240	81.0	240	76.0	255	44.9	262	0
hr.		hr.		hr.		hr.	
24	100	24	100	24	100	24	89.9
						48	97.7

Results were not reproducible for salts which were apparently neutral—i.e. for samples which when dissolved in 70% acetone solutions, gave a pH of 7.0 or more. The rate of hydrolysis varied greatly with marked inhibition periods for some salts and none for others. However, the results showed qualitatively that an increase in temperature (from 25° C. to 35° C.) eliminated the inhibition period as had the addition of sulphuric acid. The rate of hydrolysis also increased with increased sulphuric acid concentration. An increase in the water concentration increased the length of the inhibition period and decreased the rate of hydrolysis.

The presence of acid ester and of sulphuric acid accelerated the hydrolysis of the salts forms of cellulose acetate sulphate. This indicates that an exchange of sodium, potassium, etc., by hydrogen probably occurred, followed by hydrolysis of the acid ester. The acetic acid did not catalyze the hydrolysis because of the fact that acetic acid ionization was practically suppressed in acetone. Probably other strong acids which ionize in acetone, such as hydrochloric, would also act as catalysts.

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VISCOSITY - WEIGHT AVERAGE MOLECULAR WEIGHT RELATIONSHIPS FOR DEXTRANS IN THE HIGHER CLINICAL SIZE RANGE

REPRODUCIBILITY OF THE LIGHT SCATTERING METHOD[1]

By W. Donald Graham

ABSTRACT

Intrinsic viscosity of dextrans, produced by NRRL B512 *Leuconostoc mesenteroides* and degraded to the weight average molecular weight range 150,000 to 425,000, showed a highly significant correlation with weight average molecular weights. The line of best fit for the data took the form

$$[\eta] = 1.58 \times 10^{-3} M_w^{0.457}$$

and occupied a position intermediate among the lines derived in other laboratories for similar relationships in a lower molecular weight range. Under the conditions employed, repeated light scattering molecular weight determinations on the same dextran sample may be expected to fall within less than $\pm 10\%$ of the mean 95% of the time.

In Canada, clinical dextrans from the United States of America, from Great Britain, and from a domestic source are available. The American type dextran plasma expander has a weight average molecular weight, as determined by light scattering methods, of 60,000 to 80,000, while that of the Canadian type is approximately 80,000 and that of the British type falls in the range 150,000 to 200,000. The British type dextran contains a considerably greater proportion of high molecular weight material than is the case with dextrans produced in North America.

To assess the molecular sizes of dextrans some laboratories prefer to make viscosity measurements and to convert these to a calculated weight average molecular weight by means of a mathematical relationship. Several studies of the physicochemical properties of dextrans of a molecular size suitable for clinical use have been made and such mathematical relationships established. Wales and his co-workers (4) and Senti *et al.* (3) have reported that within the range of molecular sizes likely to be encountered in the American type dextran the relationship $[\eta] = 10^{-3} M_w^{0.5}$, where $[\eta]$ = intrinsic viscosity in dl./gm. and M_w = weight average molecular weight (or, more strictly speaking, viscosity average molecular weight), is a close approximation. Wolff *et al.* (5) working with similar material related inherent viscosity to M_w by the equation $\eta_i = 2.03 \times 10^{-3} M_w^{0.431}$. It has been established (2, 4) that for clinical dextran manufactured from native dextrans synthesized by NRRL B512 *Leuconostoc mesenteroides* the intrinsic viscosity is closely approximated by the inherent viscosity when measurements are made within certain concentration ranges. Mastrangelo *et al.* (1) in a similar study arrived at the relationship $\log M_w = 2.5714 \log \eta_i + 6.3998$ for American type dextrans in the weight average

[1]*Manuscript received in original form October 20, 1955, and, as revised, December 21, 1955. Contribution from the Food and Drug Laboratories, Department of National Health and Welfare, Ottawa, Canada.*

molecular weight range 60,000 to 100,000. In the higher molecular weight ranges Senti *et al.* (3) have found that the exponent a in the relation $[\eta] = KM^a$ tends to take smaller values.

From these mathematical relationships an intrinsic viscosity of 0.25 indicates a weight average molecular weight of 62,500, 70,800, or 71,000 while $[\eta] = 0.3$ indicates weights of 90,000, 108,000, and 114,000 respectively. If it be assumed that the same relationships hold, a British type dextran with an intrinsic viscosity of around 0.4 would be expected to have a weight average molecular weight of 160,000, 211,000, or 243,000, depending on which conversion factor was used.

Since this degree of uncertainty is rather high, it was decided to study the viscosity – molecular weight correlation in the higher viscosity ranges to determine which of these mathematical treatments yielded the more accurate results. In common with the previous investigators, the true weight average molecular weight was taken as that determined by a light scattering method.

METHODS

A Brice-Phoenix light scattering photometer series 1000 was employed. A solution containing approximately 1 gram of dextran/100 ml. of glass-distilled water was prepared and from this four dilutions were made to contain approximately 0.15, 0.2, 0.25, and 0.35 gm./50 ml. An ultrafine, sintered glass, pressure filter was thoroughly flushed with clean water and approximately 50 ml. of the filtered water was collected in a dissymmetry cell. The turbidity of the water was determined in the light scattering photometer using blue light λ 436 mμ. Starting with the most dilute, the dextran solutions were filtered through the same filter into a dissymmetry cell. The I_{45}/I_{135} ratio corrected for the solvent and the I_{90}/I_0 ratio were determined. If the dissymmetry ratio (I_{45}/I_{135} corrected for solvent) exceeded 1.15 the solution was refiltered. The solutions, as removed from the dissymmetry cells, were used for viscosity determinations at 25° C. using Ostwald-Cannon-Fenske viscometers series 50. In all viscometers used, efflux times for water exceeded 240 sec. The density of dextran solutions at 25° C. was taken as $0.9976+0.00393\ c$ where c = concentration in gm./100 ml. Other portions of the solutions were reserved for the determination of dextran concentration using a photoelectric Rudolph precision polarimeter with a 1 dm. tube. The specific rotation $[\alpha]_{20}^{D}$ was taken as +200°.

The turbidity data were interpreted by extrapolating the Hc/τ vs. c relationship to zero concentration by least squares whence the reciprocal of the intercept is $M_w (H = 0.624 \times 10^{-5})$. Turbidities of the dextran solutions were corrected for turbidity of the solvent, which did not exceed 5×10^{-5} cm.$^{-1}$. The viscosity data were converted to specific viscosities and the η_{sp}/c vs. c relationship was extrapolated to zero concentration by the least squares method to obtain the intercept $[\eta]$.

EXPERIMENTAL AND RESULTS

Clinical dextran samples (samples 1–6) or fractions of such samples, obtained by partial precipitation from aqueous methanol solution (samples 7–17), and

all of NRRL B512 *L. mesenteroides* origin, were analyzed by light scattering and found to have weight average molecular weights in the range 150,000 to 425,000. The intrinsic viscosities of these samples were determined at 25° C. and the data accumulated are presented in Table I. The coefficient of correlation for these data was 0.95 with $P = 0.001$. The least squares line of best fit was found to be

TABLE I

WEIGHT AVERAGE MOLECULAR WEIGHTS AND INTRINSIC VISCOSITIES OF DEXTRANS

Sample	Weight average molecular weight	Intrinsic viscosity, dl./gm.
1	150,000	0.40
2	182,000	0.41
3	182,000	0.37
4	179,000	0.39
5	221,000	0.39
6	210,000	0.41
7	294,000	0.54
8	385,000	0.55
9	370,000	0.55
10	425,000	0.57
11	372,000	0.59
12	414,000	0.59
13	185,000	0.39
14	206,000	0.45
15	172,000	0.41
16	357,000	0.56
17	334,000	0.53

$$[\eta] = 1.58 \times 10^{-3} M_w^{0.457}.$$

These experimental points and the line of best fit (curve B) have been plotted in Fig. 1. The scatter of the data is influenced to a considerable extent by the precision of the methods involved. It should be borne in mind that a difference in intrinsic viscosity of 0.01 dl./gm. is equivalent to a difference in the calculated viscosity average molecular weight of more than 5% at 150,000 and more than 8% at 425,000. The scatter of the experimental data is influenced too by the degree of homogeneity of the polymer sample and by the skewness of the distribution of the various molecular sizes in the polymer. The three points in Fig. 1 which lie above curve A and below curve C all were obtained on clinical dextran preparations which contain a much wider range of molecular sizes than the fractions obtained therefrom.

In Fig. 1 are represented, over the molecular weight range under consideration, the log–log plots of the relationships between intrinsic viscosity and weight average molecular weight found in the present and previous investigations. It may be seen that in this range the present curve occupies an intermediate position. It would appear that either the relationship $[\eta] = 10^{-3} M_w^{0.5}$ or $\eta_i = 2.03 \times 10^{-3} M_w^{0.431}$ would yield an approximate M_w in the higher ranges of $[\eta]$ although the correct relation probably occupies an intermediate position.

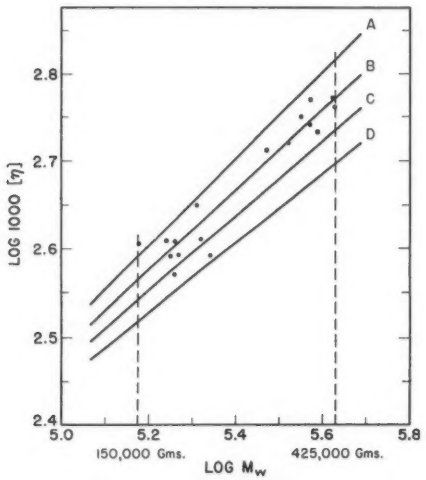

FIG. 1. Mathematical relationships between intrinsic viscosity and weight average molecular weight of B512 dextrans.
Curve A—Wales and co-workers, Ref. 4.
Curve B—Present study.
Curve C—Wolff *et al.*, Ref. 5.
Curve D—Mastrangelo *et al.*, Ref. 1.
The points in the figure represent the data from which curve B was derived.

Under the conditions of these experiments the relationship reported by Mastrangelo *et al.* (1) does not fit the data satisfactorily.

While the use of viscosity measurements to obtain calculated average molecular weights is not likely to be entirely adequate for analytical control of the final product in dextran plasma expander production, the measurement of inherent viscosity is useful during earlier stages of manufacture. The conversion of such values to average molecular weights must be considered only as an approximation.

APPENDIX

REPRODUCIBILITY OF WEIGHT AVERAGE MOLECULAR WEIGHT DETERMINATIONS BY LIGHT SCATTERING ON DEXTRAN PLASMA EXPANDERS

In any enforcement program the reproducibility of the analytical results obtained by a particular method should be established. Only with this information available can a satisfactory conclusion be reached with regard to borderline cases. With this in mind, a study of the reproducibility of dextran plasma expander weight average molecular weight determinations by light scattering, as practiced in this laboratory, was undertaken.

Over a period of about six months, as time permitted, repeat assays were performed on dry, well blended samples of dextrans of four different mean molecular sizes within the weight range likely to be encountered in day to day

analyses. The analytical procedure employed was essentially that outlined above. The results of these analyses are presented in Table II together with some statistics computed from the analytical data.

TABLE II

REPRODUCIBILITY OF LIGHT SCATTERING MOLECULAR WEIGHT DETERMINATIONS

	Sample number			
	1	2	3	4
	Weight average molecular weight			
	72,600	161,000	265,000	341,000
	71,800	166,000	268,000	374,000
	70,400	155,000	285,000	335,000
	71,700	167,000	275,000	376,000
	70,700	167,000	256,000	351,000
	72,900	161,000	271,000	355,000
	71,400	170,000		363,000
	71,100	162,000		353,000
	72,700	173,000		
	72,100			
Mean	71,700	165,000	270,000	356,000
Range as % of mean	3.5	10.9	10.6	11.6
Standard error of a single determination as % of mean	1.2	3.3	3.6	4.1
95% confidence limits of a single determination as % of mean	3.7	7.5	9.3	9.7

These results compare favorably with those of Riddick *et al.* (2) whose data have been recalculated to give the standard errors of single determinations as percentages of the means for three samples analyzed 10, 16, and 9 times as 3.2, 3.7, and 7.2 respectively. Under the conditions employed in this laboratory, repeated determinations on the same dextran sample may be expected to fall within less than $\pm 10\%$ of the mean, 95% of the time.

ACKNOWLEDGMENT

The assistance of Miss Odette Patry in this work is gratefully acknowledged.

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A THERMOCOUPLE CONNECTION OPERATED BY REMOTE CONTROL

By A. C. Burr and D. J. Neil

Frequently it is necessary to monitor or observe the temperature of a specimen within a vacuum system and in many cases it is desirable to make or break the thermocouple for manipulation of the specimen. Such a need arose in our laboratory and the purpose of this note is to describe the solution which was devised.

Fig. 1 shows the experimental arrangement with the specimen, *A* (a circular cylinder $1\frac{1}{2}$ in. long by $\frac{1}{2}$ in. diameter), suspended vertically within the vacuum system by a fine nichrome wire, *B*. This wire was peened into a small hole drilled into the end of *A*. The other end of *B* was connected to a steel counterpoise which could be manipulated externally by a permanent magnet.

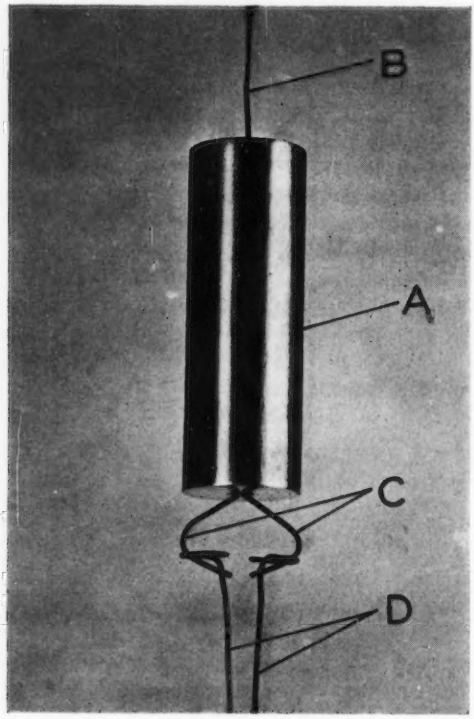

Fig. 1. Model of the thermocouple connection operated by remote control.

The bead of a chromel–alumel thermocouple was peened into a small hole drilled into the bottom of *A*. The thermocouple *C* was then cut off and formed into the shape shown in the figure. When the thermocouple circuit was to be "made", the assembly *A*, *B*, and *C* was lowered with the counterpoise until *C* was observed to be seated properly in the stationary chromel–alumel leads *D*. These fixed leads were shaped as shown in the figure to receive the thermocouple *C*, and were sealed into the vacuum system at their opposite ends. Care was taken to ensure that the polarity was correct; to do this a trial was made prior to evacuation of the system.

The suspension system for the specimen was so arranged that it could be easily rotated through 180° by means of a greased standard taper seal.

In order to prevent the separation of the leads, *D*, under the influence of the load applied through *C*, they were fastened together with Pyrex glass (not shown in the figure). When the connection was "made" the elastic deformation of *C* ensured a relatively good electrical joint.

The efficiency of this connection was determined by comparing the temperature observed through the arrangement *C–D* with that indicated by an auxiliary thermocouple peened into *A* at another location. It was found that the temperature of *A* could be observed or controlled through this connection within ±2° in the neighborhood of 500° C.

Received November 23, 1955.
Aluminium Laboratories Limited,
Kingston, Ontario.

A USEFUL MODIFICATION OF THE HERSHBERG MELTING POINT APPARATUS

By George F Wright

A modification of the Thiele tube has been devised by Markley and improved by Hershberg (4, 3) for the determination of precise capillary melting points. This apparatus has been found to have general applicability in the organic chemical laboratory and its usefulness is reflected in reports of several modifications (6, 5, 1, 2, 8). Other elaborations are described in the present publication.

Not all of the previously suggested alterations have been found to be useful in the Toronto Laboratory. Specifically the replacement of sulphuric acid by silicone fluid has been found to be disadvantageous because of the tendency with age for the viscosity of the silicone oil to increase. In this circumstance bubbles are likely to be formed by stirrer action and these bubbles obstruct the view of the sample tube. This fault is only partially obviated by extension of the stirrer guide below the level of the circulating liquid.

Of course sulphuric acid also is troublesome because of its relatively high volatility, especially when it has accumulated atmospheric moisture. Saturation of the acid by potassium sulphate decreases the volatility but the bath

tends to solidify at room temperature because of the limited solubility of this potassium salt. This trouble is not encountered if a solution (10–11%) of lithium sulphate in sulphuric acid is used as the circulating medium. Such a bath will tolerate the small amounts of sodium or potassium nitrate which may be added from time to time in order to remove color.

In the opinion of the author the chief disadvantage of the Hershberg apparatus is an indirect result of its otherwise advantageous uniformity of temperature distribution, which is largely brought about by vigorous stirring. This strong circulation tends to dislodge sample tubes from capillary attraction to the thermometer unless they are (inconveniently) secured tightly to it by a plastic band. The alternative suspension of the sample tubes from a cap surrounding the thermometer was originally specified by Hershberg, but it is difficult to prevent motion of the melting point capillary tube by this device, which at any rate can conveniently accommodate only two tubes. Since a mixture melting point determined with precision should involve known, unknown, and at least one mixture, the Hershberg tube holder is inadequate in this respect. A commercial tube holder comprised of glass loops attached to the thermometer is not a satisfactory alternative because the three sample tubes which it holds are widely separated in the line of sight. Furthermore such thermometers tend to suffer damage because of thermal strain and thus may be lost after careful standardization.

In Fig. 1 is shown a sample holder which during 10 years has proved to be

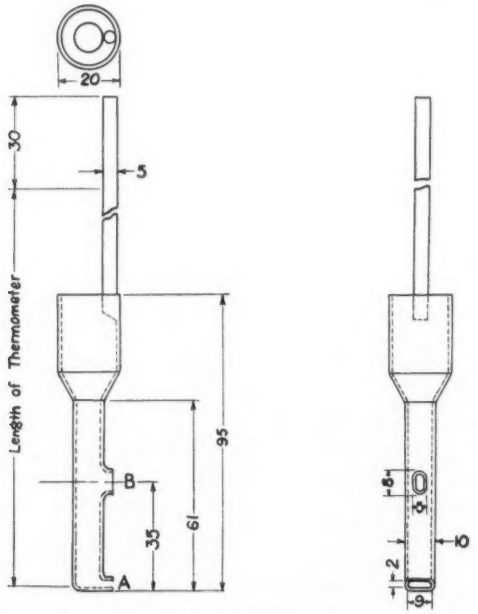

FIG. 1. Sample holder for use in Hershberg apparatus. 24 mm. I.D., total height 160 mm., acid height 120 mm. Note: All dimensions in mm.

useful in the author's laboratory. The dimensions of this device must be accommodated to the diameter of the 0° to 360°–400° thermometer which, in the present instance, is 6 mm. All dimensions being O.D., a 20 mm. Pyrex tube is sealed concentrically in a 10 mm. tube and the bottom of the latter is drawn laterally, after a narrow zone has been heated, by a quick sidewise motion which precludes optical distortion on one side. Subsequently the drawn portion is broken off and fire-polished as is shown at *A* (Fig. 1). Above this bottom vent at a distance of about 35 mm. the tube wall is drawn thin and finally broken through to furnish a second larger vent. In line with these two vents is then attached a 5 mm. glass rod of such length that it extends 30 mm. beyond the top of the thermometer when the latter is resting on the bottom of the 10 mm. portion of the assembly. By means of a graphite, or graphite-coated steel, rod inserted in the 10 mm. tube, this 5 mm. glass rod may be sealed so that its wall is coincident with the linear extension of that side of the inner wall of the 10 mm. tubing at which the two vents *A* and *B* have been situated.

The back of the thermometer may then be secured by wire-wrapping to the top and bottom of the 5 mm. tube. The top wrapping may be of fine nichrome or stainless steel but the bottom should be of platinum in order to obviate corrosion by the bath. The assembly may then be suspended from the upper 30 mm. of the 5 mm. glass rod so that it stands at the proper height in the Hershberg apparatus. If a thermometer engraved for 100 mm. immersion has been chosen, the readings at room temperature are discernible.

The space between the front of the thermometer and the inner wall of the front of the 10 mm. tubing will accommodate as many as five melting point tubes in parallel contact with one and another. To some it may seem disadvantageous that sample tubes must be chosen which do not exceed in diameter the fixed space in which they are to be inserted. Those who agree with the author that precision of melting point determination is dependent on sample tube diameter will not object to this limitation although they may question the practicability of sample tube fabrication to the necessary tolerance.

The author prepares melting point capillaries for his apparatus by sorting with a "go-no go" gauge the vaccine capillary tubing No. 46485 with 0.15 mm. average wall thickness, 0.75–1.00 mm. in outside diameter, 34 in. long, obtained from Owens-Illinois Inter-America Corp., Toledo, Ohio. The wastage of about 50% which occurs by choice of 0.8–0.9 mm. diameter tubing is probably no greater than that which obtains by hand-drawing of melting point capillaries. Furthermore the uniformity in length of the purchased tubing facilitates the double-ended sealing of tubes 150 mm. long under conditions where flame moisture is avoided inside the tube. Consequently such tubes are dry until such time as they may be cut into two melting point capillaries by means of a carborundum crystal.

Of course the arrangement of the thermometer in this sample holder tends to vitiate the significance of calibration since immersion to the specified mark usually is not possible. However the author believes that a thermometer should always be calibrated in respect of the melting point apparatus in which

it is to be used. In consequence a series of carefully purified reliable standard substances are used for such calibration. The substances selected for this purpose in the author's laboratory are as follows:—

Phenylpropionic acid	m.p. 48.7°	Benzoic acid	m.p. 123.5°
Naphthalene	m.p. 80.1°	Salicylic acid	m.p. 157.5°
m-Dinitrobenzene	m.p. 89.9°	Triphenylcarbinol	m.p. 162.4°–162.9°
Triphenylmethane	m.p. 93.2°		
Phenanthrene	m.p. 99.9°	Anisic acid	m.p. 183°
o-Toluic acid	m.p. 108°	Anthracene	m.p. 216°
Anthraquinone	m.p. 286°	*p*-Bromobenzoic acid	m.p. 242.4°

The purity of these standards has been attested by no more than one-quarter degree of prior softening in the Rheinboldt thaw point apparatus (7). Such standards should always be vacuum-dried shortly before they are to be used for standardization.

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Received November 9, 1955.
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A MIXTURE AND METHOD FOR MAKING TOUGH POROUS UNIFORM SPHERES

By L. R. Galloway[1] and N. Epstein

An investigation is now being conducted at the University of British Columbia to determine the effect of packing geometry on particle surface to fluid heat and mass transfer in stacked beds of spheres. An air–water system is being used to measure the transfer rates, the water being evaporated from the surface of porous spheres to an air stream, in the constant rate period of drying. In order to hold constant all packing characteristics except geometrical configuration, it was necessary to use perfectly spherical balls which were uniform in size and surface roughness and which were not subject to attrition. High internal porosity of the spheres was another requirement in order to have a long, constant rate drying period. Machineability was also desired since each sphere was drilled and pinned to a neighboring sphere to form a rigid bundle of spheres. No commercial packing or catalyst carrier was found

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that embodied all these characteristics and it was therefore necessary to develop a mixture and a method of fabrication that satisfied these requirements best.

A satisfactory mixture was found to have the following composition:

50.0 weight % Celite (supplied by Johns Manville Company),
37.5 weight % Alundum Cement RA 305 (supplied by Central Scientific Company, No. 11461B),
12.5 weight % Colloidal Kaolin (supplied by Merck Company),
130 milliliters water per 100 grams dry solids.

Repeated trials to mold whole spheres were unsuccessful and the most satisfactory method found was to mold half spheres and join two halves to make a whole sphere. Molds were made in an aluminum plate by drilling with a $\frac{3}{4}$ in. rotary file to a depth slightly greater than $\frac{3}{8}$ in. This produced a hole hemispherical in shape, which was buffed with a fine abrasive to remove the rough cutting marks of the file.

Following is the method used to fabricate the spheres. The mold was greased sparingly with valvoline stopcock grease and the wet clay mixture was carefully placed in the mold in such a way that no air was entrapped. The mold was then placed in a laboratory oven at approximately 250° F. in order to dry out the wet clay mixture. Because the clay, when dried thoroughly, had a tendency to stick in the mold, it was removed from the mold when it became rigid but while it still remained in a moist condition, and it was then dried thoroughly. From the oven the clay half sphere was transferred to an electric furnace controlled at 1000° C. and was fired for approximately four hours. At the end of four hours it was cooled slowly in the furnace over a period of about 14 hours. When cool, the flat side of the half-sphere was ground down until a perfect half-sphere was formed, as determined by measuring with a micrometer. Two halves were joined together with Araldite AN-104, a cold setting organic resin, to form a whole sphere.

The spheres which resulted were found to have an average diameter of 0.673 in. with a standard deviation from the mean of 0.004 in. The amount of water used in mixing the dry solids was accurately measured to the nearest milliliter because variations in the amount of water used greater than 1 milliliter were found to cause the diameter of the resulting sphere to vary considerably.

Internal porosity of the spheres was measured as 67%. There was no deterioration in balls immersed for long periods in both hot and cold water.

ACKNOWLEDGMENT

The authors are indebted to the National Research Council of Canada for its continuing financial assistance of the momentum, heat, and mass transfer studies, in the course of which the present technique was developed.

RECEIVED NOVEMBER 3, 1955.
DEPARTMENT OF CHEMICAL ENGINEERING,
UNIVERSITY OF BRITISH COLUMBIA,
VANCOUVER, B.C.

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Printed in Canada *by* University of Toronto Press

CANADIAN JOURNAL OF TECHNOLOGY

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